



I L L I N O I S

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

-

PRODUCTION NOTE

University of Illinois at  
Urbana-Champaign Library  
Large-scale Digitization Project, 2007.



# UNIVERSITY OF ILLINOIS BULLETIN

ISSUED WEEKLY

Vol. XVIII

February 21, 1921

No. 25

[Entered as second-class matter December 11, 1912, at the post office at Urbana, Illinois, under the Act of August 24, 1912. Acceptance for mailing at the special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 31, 1918]

---

## SOME CONDITIONS AFFECTING THE USEFULNESS OF IRON OXIDE FOR CITY GAS PURIFICATION

BY

WM. A. DUNKLEY

ILLINOIS COAL MINING INVESTIGATIONS COÖPERATIVE AGREEMENT

(THIS REPORT WAS PREPARED UNDER A COÖPERATIVE AGREEMENT BETWEEN THE  
ENGINEERING EXPERIMENT STATION OF THE UNIVERSITY OF ILLINOIS,  
THE ILLINOIS STATE GEOLOGICAL SURVEY, AND  
THE U. S. BUREAU OF MINES)



BULLETIN No. 119

ENGINEERING EXPERIMENT STATION

PUBLISHED BY THE UNIVERSITY OF ILLINOIS, URBANA

---

EUROPEAN AGENT

CHAPMAN & HALL, LTD., LONDON

THE Engineering Experiment Station was established by act of the Board of Trustees of the University of Illinois on December 8, 1903. It is the purpose of the Station to conduct investigations and make studies of importance to the engineering, manufacturing, railway, mining, and other industrial interests of the State.

The management of the Engineering Experiment Station is vested in an Executive Staff composed of the Director and his Assistant, the Heads of the several Departments in the College of Engineering, and the Professor of Industrial Chemistry. This Staff is responsible for the establishment of general policies governing the work of the Station, including the approval of material for publication. All members of the teaching staff of the College are encouraged to engage in scientific research, either directly or in coöperation with the Research Corps composed of full-time research assistants, research graduate assistants, and special investigators.

To render the results of its scientific investigations available to the public, the Engineering Experiment Station publishes and distributes a series of bulletins. Occasionally it publishes circulars of timely interest, presenting information of importance, compiled from various sources which may not readily be accessible to the clientele of the Station.

The volume and number at the top of the front cover page are merely arbitrary numbers and refer to the general publications of the University. *Either above the title or below the seal* is given the number of the Engineering Experiment Station bulletin or circular which should be used in referring to these publications.

For copies of bulletins or circulars or for other information address

THE ENGINEERING EXPERIMENT STATION,  
UNIVERSITY OF ILLINOIS,  
URBANA, ILLINOIS.



UNIVERSITY OF ILLINOIS  
ENGINEERING EXPERIMENT STATION

---

BULLETIN No. 119

FEBRUARY, 1921

---

SOME CONDITIONS AFFECTING THE USEFULNESS  
OF IRON OXIDE FOR CITY GAS PURIFICATION

BY  
WM. A. DUNKLEY  
STATE GEOLOGICAL SURVEY DIVISION

ENGINEERING EXPERIMENT STATION

PUBLISHED BY THE UNIVERSITY OF ILLINOIS, URBANA

**This page is intentionally blank.**

## CONTENTS

	PAGE
I. INTRODUCTION . . . . .	7
1. Purpose of Investigation . . . . .	7
2. Acknowledgments . . . . .	8
II. THE PURIFYING PROCESS . . . . .	9
3. Chemical Reactions . . . . .	9
4. Method of Application . . . . .	10
III. OXIDES FOR GAS PURIFICATION . . . . .	11
5. Sources of Oxides . . . . .	11
6. Activity and Capacity of Oxides . . . . .	11
Primary Capacity . . . . .	12
Ultimate Capacity . . . . .	12
Activity . . . . .	13
IV. THE TESTING OF OXIDES . . . . .	15
7. Chemical Analysis . . . . .	15
8. Testing Oxides with Pure Hydrogen Sulphide . . . . .	15
9. Testing Oxides with Unpurified City Gas . . . . .	17
10. Choice of Testing Method . . . . .	17
V. TESTING METHOD EMPLOYED IN PRESENT INVESTIGATION . . . . .	19
11. Information Desired . . . . .	19
12. Method Employed . . . . .	19
13. Oxides Tested . . . . .	20
VI. PREVIOUS WORK . . . . .	24
VII. EFFECT OF WATER CONTENT ON BEHAVIOR OF OXIDES . . . . .	26
14. Hydration of Iron Oxides . . . . .	26
15. Effect of Water Content of Various Oxides on their Relative Activities and Capacities . . . . .	28
Determination of Water Content . . . . .	28
Preparation of Samples for Drying . . . . .	29
Drying of Samples . . . . .	30
Activity and Capacity of Dried Samples . . . . .	30
16. Effect of Varying Water Content on the Behavior of Different Oxides . . . . .	31
17. Function of Water Present . . . . .	35

	PAGE
18. Rehydration of Oxides . . . . .	36
19. Effect of Sulphiding and Revivifying on the Water Content of Oxides . . . . .	38
VIII. ACTIVITY AND CAPACITY OF OXIDES AFTER REVIVIFICATION	40
IX. EFFECTS OF CONDITIONS OF PREPARATION ON ACTIVITY OF OXIDES . . . . .	43
X. PREPARATION OF COMMERCIAL OXIDES . . . . .	49
20. Natural Oxides . . . . .	46
21. Precipitated Oxides . . . . .	47
22. Rust Oxides . . . . .	48
Oxidation by Rusting Solutions . . . . .	48
Oxidation by Water . . . . .	50
23. Pyritic Cinder . . . . .	50
XI. CHOICE OF OXIDE . . . . .	52
XII. SUMMARY OF CONCLUSIONS . . . . .	56

## LIST OF FIGURES

NO.		PAGE
1.	Kunberger Apparatus for Testing Oxides for Gas Purification . . .	16
2.	Decomposition of Hydrogen Sulphide by Various Iron Oxides during Successive Minutes of Sulphiding . . . . .	20
3.	Activities and Capacities of Various Oxides after Drying to Constant Weight . . . . .	31
4.	Effect of Water Content upon Activity and Capacity of Oxides . . .	33
5.	Effect of Drying and Remoistening upon the Activity of an Iron Oxide	36
6.	Activities and Capacities of Three Typical Oxides during Four Successive Foulings . . . . .	41

## LIST OF TABLES

NO.		PAGE
1.	Sulphiding Properties of Various Oxides . . . . .	21
2.	Water Content and Sulphiding Properties of Various Oxides after Drying to Constant Weight . . . . .	32

**This page is intentionally blank.**



## SOME CONDITIONS AFFECTING THE USEFULNESS OF IRON OXIDE FOR CITY GAS PURIFICATION

### I. INTRODUCTION

1. *Purpose of Investigation.*—This bulletin is a report of work carried on under a coöperative agreement participated in by the Illinois State Geological Survey Division, the Engineering Experiment Station of the University of Illinois, and the U. S. Bureau of Mines. The purpose of this coöperation is to investigate resources, mining methods, and the application to industrial and domestic uses of coals of the central coal mining district.

The gas and coking industry uses a large amount of coal, and many attempts have been made to increase the application of coals of the central district to the industry in this region. The use of central district coals for gas making presents many problems, of which the purification of the gas from hydrogen sulphide derived from the coal is an important one.

The present overloaded condition of the gas-purifying equipment in many gas plants, brought about by economic conditions during the past few years, has increased the interest attaching to gas purification. Purifying conditions in several plants have become critical on account of the greatly increased gas production and the generally higher sulphur content of the fuels used for gas making. The financial condition of many gas companies practically prohibits the installation of larger equipment. The only solution of the problem for the present, therefore, lies in the more efficient use of existing equipment. That there is much room for improvement in this department of gas manufacture was shown in Bulletin 25 of the Coöperative Mining Series, published by the Illinois State Geological Survey. In that bulletin the purifying conditions in the medium-size gas plants of Illinois were discussed and certain improvements in operating methods were suggested, but it was pointed out that more information was needed relative to the properties of various types of oxide of iron, which have been used during many years for purifying gas. The purpose of the present report is to summarize the existing information on this sub-

ject and to discuss some experiments which have been made recently in the effort to explain some of the observed facts concerning purifying oxides.

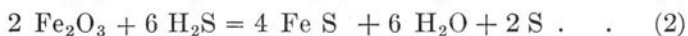
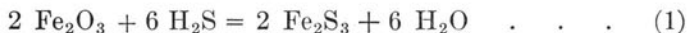
2. *Acknowledgments.*—Thanks are due to several iron oxide producing companies for supplying samples of material for study. Among these contributors are the H. C. Frick Coke Company, the Connelly Iron Sponge and Governor Company, the Iron Hydroxide Company, the American Mineral Products and Color Company, the Alpha-Lux Company, the Pennsylvania Salt Company, the Gas Purifying Materials Company, and the Henderson Lumber Company.

C. H. STONE of the Rochester (New York) Railway and Light Company, DR. A. R. POWELL of the U. S. Bureau of Mines, J. R. CAMPBELL of the H. C. Frick Company, H. O. ANDREW of the Springfield (Massachusetts) Gas Light Company, and Professors W. A. NOYES and E. W. WASHBURN of the University of Illinois, have given valuable suggestions relative to certain phases of the work. Much of the chemical analysis work was performed by C. E. BARNES, Research Assistant in Gas Engineering at the University of Illinois.

## II. THE PURIFYING PROCESS

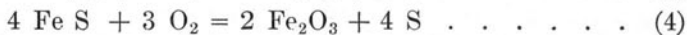
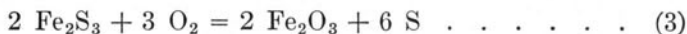
3. *Chemical Reactions.*—The purification of city gas, in the restricted sense in which the term “purification” will be used here, is the removal of hydrogen sulphide from the gas before distribution to the consumer. This has been accomplished for many years by some form of iron oxide.

Several primary and secondary reactions may take place in the gas purifiers under different conditions of operation. The following equations probably represent fairly well the sulphiding process:



Some writers include one or more molecules of water in the formula for iron oxide, assuming, for example, that the iron oxide is present as ferric oxide monohydrate ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). While a certain amount of water seems to be necessary in order that the ferric oxide may react with hydrogen sulphide, the indications are, as will be discussed later, that an amount of water corresponding to the monohydrate is not necessary to the reaction. It seems likely that the water present exerts a catalytic effect, influencing the speed of reaction, rather than actually entering into it.

If a good purifying material, after sulphiding, be exposed to the air, the sulphides react with the oxygen of the air and iron oxide (ferric) is regenerated. This process is usually termed revivification and has a very important bearing upon the usefulness of an oxide for gas purification. The chemical reactions occurring during the revivification process are not thoroughly understood but they are usually represented by the following equations:



Several secondary reactions may also take place under certain conditions. Which of the four primary reactions shown in the above

equations will occur in a particular case is determined, doubtless, by the conditions prevailing at the particular time. Just what conditions affect these reactions has not been determined for certain, though temperature, condition of acidity or alkalinity, etc., may be factors. Recent investigations by Weyman seem to indicate that equation (1) represents the more favorable sulphiding reaction, since the reaction of equation (3) probably goes more rapidly than that of equation (4). None of these reactions goes entirely to completion in practice. The extent to which these processes may be repeated and the completeness during successive repetitions are most important factors in determining the value of a material for purifying gas, and vary greatly with different commercial materials.

4. *Method of Application.*—For those who are not familiar with the purifying process, it may be said that the purification of gas is accomplished in a series of large receptacles termed “boxes,” in which the iron oxide, mixed with wood-planer chips, ground corn cobs, sawdust, blast-furnace slag, or other porous material is spread in layers from 2 to 6 feet in thickness on wood grids. A purifier box may contain one or more layers of the mixture, usually two layers in present practice. The gas enters beneath the layers and passes through them. Sometimes the gas flow is divided, the gas entering between two layers, part of the gas passing up through one layer and part down through the other; or the gas may enter below the lower layer and above the upper layer and passing through the layers find its exit through a connection to the box between the layers. Usually in divided flow boxes the direction of flow is reversible. There may be only two purifier boxes in series, or there may be six or eight. The oxide in the first box usually does by far the largest part of the purification. The hydrogen sulphide remaining in the gas after it passes through the first box is removed in gradual stages by the subsequent boxes.

The reactions (3) and (4), called the revivifying reactions, may be accomplished either by removal of the sulphided material from the purifying boxes and exposure to the air, or by introducing air into the material in place, either by admitting a small percentage of air to the gas, or by forcing air through the sulphided material in a purifier from which the gas has been turned off.

### III. OXIDES FOR GAS PURIFICATION

5. *Sources of Oxides.*—The oxides employed in gas-plant practice may be divided into four general classes:

- (1) Oxides existing in nature as ore deposits.
- (2) Oxides produced from metallic iron by rusting, either with or without the use of agents which accelerate the rusting process.
- (3) Precipitated oxides, which are obtained directly from solutions of iron salts, either as primary products or as by-products of some manufacturing process.
- (4) The oxide resulting from burning pyrites for sulphuric acid manufacture.

The choice of material has been governed in the past chiefly by price considerations and this is still an important factor. Personal preference, caused by fortunate or unfortunate experiences with particular oxides, also governs the selection in some cases. There is probably no material used in the gas-making process about which more extravagant claims have been and are made by certain producers than purifying oxide. Considering the general lack of facilities for testing oxide in the average gas-plant, it is little wonder that purifying oxides have been purchased rather blindly by gas operators, with later disappointment when the claims of the oxide companies were not borne out, as has frequently happened. It can be stated, from operating experience as well as from laboratory tests, that good oxides of each type are available, and the real problem is the selection of the material best suited to a particular case.

6. *Activity and Capacity of Oxides.*—Sufficient distinction has not been made in the past between the rapidity or activity of oxides in the absorption of hydrogen sulphide, and the primary and ultimate capacity of these materials. The average gas operator calls an oxide "active" when it absorbs a fair percentage of hydrogen sulphide, indeed, the term "active" is often used to indicate merely the ability to absorb hydrogen sulphide without reference to rapidity or capacity.

The failure to distinguish between these characteristics is not surprising since there are no well-defined standards of performance with which to compare the behavior of a particular sample.

Possibly, in the past, under average operating conditions no careful distinction was necessary. If a particular material was capable of absorbing a high percentage of hydrogen sulphide, the rapidity of the absorption was of secondary consideration. With overloaded conditions, however, the velocity of travel of the gas through the purifiers has increased greatly. In some cases more than ten per cent of the total daily gas production is purified during the hour of maximum production, so that at such times gas may be passing through the oxide mass at from two to three times the average rate. Chemical reactions require a finite though frequently very brief time for their completion, and in gas purification the time element becomes very important, especially after a portion of the purifying material has become sulphided. A considerable period of contact may then be necessary for the complete removal of the hydrogen sulphide by the remaining active material.

While it is believed that no formal definitions of these characteristics of purifying oxides have been accepted by the gas industry, the following will be used for the purposes of this report:

#### **Primary Capacity**

The primary capacity of an oxide for purifying gas may be defined as the ratio of the weight of hydrogen sulphide gas which a certain weight of the oxide decomposes until completely sulphided without any revivification, to the weight of hydrogen sulphide which theoretically would be decomposed by the same weight of actual ferric oxide ( $\text{Fe}_2\text{O}_3$ ). For example, one gram of pure ferric oxide theoretically would combine with 0.639 gram of hydrogen sulphide; therefore, if a gram of a particular material during complete sulphiding absorbs say 0.30 gram of hydrogen sulphide, the primary capacity is, according to the above definition, 46.9 per cent.

#### **Ultimate Capacity**

The ultimate capacity of a purifying oxide may be defined as the ratio of the weight of hydrogen sulphide which is decomposed by a certain weight of the oxide, during repeated sulphidings alternated



with revivifications, to the weight of hydrogen sulphide which would theoretically be decomposed by the same weight of pure ferric oxide ( $\text{Fe}_2\text{O}_3$ ) during one complete sulphiding, without revivification.

In tests designed to indicate the value of oxides, the ultimate capacity of the material is seldom if ever determined, since it is affected by so many variable conditions, and would require so long a time for absolute completion, that the results obtained would hardly be worth while. It is often customary to determine the capacity for four, six, ten, or in some cases even more sulphidings, or "foulings." During the later foulings the percentage of hydrogen sulphide absorbed is usually so small as to be negligible. In cases of actual operation, where revivification by removing the sulphided material to the open air is practised, the labor of handling the material out of and into the purifiers is considerable and costly. The careful operator will not return a batch of material to the purifier after revivification unless it gives promise of absorbing sufficient hydrogen sulphide during the subsequent fouling to make its handling profitable. In practice it seldom pays to return a batch to the purifiers more than four or five times, since the tar and other impurities usually present in the gas, together with the free sulphur resulting from the repeated revivifications, usually render it unfit for further use by the time it has given that amount of service. While a long series of tests may give some indication of the regenerating powers of the material, such tests are of little value in showing the ultimate capacity of the material in practice. A laboratory test may give an ultimate capacity of several hundred per cent, but the actual capacity obtainable in practice under most favorable conditions will usually be considerably less, probably not over 200 per cent. While the ultimate capacity of a material is an uncertain quantity and cannot be predicted, the idea involved in such a conception must be kept in mind in the evaluation of any material for commercial use.

#### Activity

The relation of activity, or rapidity of action, of an oxide to its commercial value has not been definitely determined. Formulas for the design of gas purifiers sometimes take this factor into account indirectly, but none of them include an individual activity factor, because no such factors for oxides have been worked out. It is a fact well recognized among gas manufacturers that gas of a given hydrogen

sulphide content can be passed much more rapidly through some oxides than through others, with complete removal of the hydrogen sulphide. This fact becomes all the more important in the operation of the catch box, by which term is designated a purifier placed in a fixed position (relative to sequence of operation) at the end of a series of purifiers, to remove the last traces of hydrogen sulphide which may pass the other, changeable-sequence purifiers. The hydrogen sulphide content of the gas entering the catch box is usually not more than 10 to 20 grains per 100 cubic feet of gas, and, where the preceding purifiers are so operated that only this small amount passes them, the active life of the catch box oxide is usually quite long. The quality and condition of the oxide in the catch box have a very important effect on its usefulness for this purpose. It is frequently observed that an oxide which will remove 90 per cent of the sulphide present in gas containing say 100 grains of hydrogen sulphide per 100 cubic feet of gas, will not completely purify gas containing only 10 grains of hydrogen sulphide per 100 cubic feet. According to the law of mass action, the rate of a chemical reaction is in proportion to the masses of the active constituents present. Therefore, the rapidity of the reaction between an oxide and hydrogen sulphide decreases with decreasing concentration of hydrogen sulphide. However, experience shows that there are marked absolute differences in the rapidities of oxides which must be taken into consideration if their relative values are to be compared. It is believed that no serious attempt has been made hitherto to establish a standard of comparison in respect to this factor. A tentative test for comparing the rapidities of oxides is described later. The measure of activity adopted for the purposes of this report is the weight of pure dry hydrogen sulphide gas which is decomposed by a given weight of the material under test in one minute, per unit of actual ferric oxide present in the same weight of material, an excess of hydrogen sulphide being present throughout the test. This measure of activity was employed only for purposes of comparison in laboratory tests, chiefly on new materials. To what extent it would indicate the behavior of oxides in practice has not yet been determined.

## IV. THE TESTING OF OXIDES

7. *Chemical Analysis.*—The value of a material for purifying gas might be expected to be in proportion to the amount of iron oxide contained in the material. The primary capacity of a material containing 60 per cent of ferric oxide, other things being equal, would be greater than the capacity of a material containing only 30 per cent. In the attempt to predict the value of a material, chemical analysis to determine ferric oxide content was formerly much employed. In the analyses of rust oxides, which almost invariably contain some unoxidized iron, magnetic separation of the free iron, or its solution by ammonium copper chloride, or a combination of the two methods, was first carried out. After the treatment it was assumed that the iron remaining in the residue was in the form of the hydrated oxide of iron ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). It was soon found, however, that although the analytical determination of hydrated oxide of iron might indicate to a certain extent the relative value of two rust oxides, it was of little value in comparing oxides of different types. Frequently a material of comparatively low iron oxide content would give much better results, even on the first fouling, than a material containing twice as much iron oxide, and the difference in behavior would frequently become more marked during further use. It soon became evident that the only way to predict the value of a material was to actually sulphide it on a small scale.

8. *Testing Oxides with Pure Hydrogen Sulphide.*—One method consisted in fouling a small weighed sample, usually 4 or 5 grams, with pure dry hydrogen sulphide gas, the apparatus being so arranged that the water formed by the decomposition of the hydrogen sulphide and oxide was retained by granulated calcium chloride in a tube which could be weighed on a chemical balance. The apparatus devised by A. F. Kunberger of the United Gas Improvement Company of Philadelphia, is the most convenient for this purpose. The arrangement of the Kunberger apparatus is shown in Fig. 1. Hydrogen sulphide gas is generated in the Kipp gas generator A; by the action of hydro-

chloric or dilute sulphuric acid upon iron sulphide. The rate of gas production and use is controlled by the stop-cock B. The gas is dried by passing through the U-tube C, containing granulated fused calcium chloride. Tube D contains 4 or 5 grams of the oxide to be tested, mixed with 2 grams of coarse sawdust. When but one fouling of the material

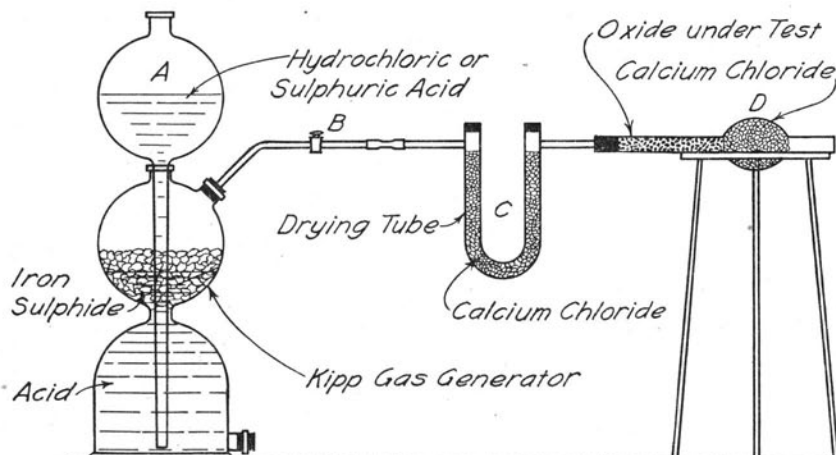


FIG. 1. KUNBERGER APPARATUS FOR TESTING OXIDES FOR GAS PURIFICATION

is to be made, the calcium chloride for retaining the water of decomposition is placed in the bulb of D, separated from the oxide and held in place by loose wads of glass wool. When several successive foulings of the oxide are to be made, it is better to have the calcium chloride in a separate tube following D. In this case the extra tube is weighed with tube D. To make the test, a weighed sample of the oxide is mixed with the sawdust and put into tube D. Tube D and the extra tube (if one is used) are then weighed together. Hydrogen sulphide gas is passed slowly through the apparatus for one hour, after which the tubes are weighed again. The gain in weight is equal to the weight of hydrogen sulphide decomposed. The oxide may be revived by passing a current of air, previously moistened by bubbling through water, through tube D. Revivification is indicated by the change of color of the material from the black of iron sulphide to the reddish-brown of iron oxide. During revivification the extra calcium chloride tube is disconnected. After revivification appears complete, another fouling is made, the weight of the tubes before and after fouling being determined as in the original experiment. The process may be re-

peated any desired number of times. The test is convenient, comparatively rapid, and gives considerable information relative to the characteristics of the material under test.

9. *Testing Oxides with Unpurified City Gas.*—Some gas chemists feel that the fouling of oxide with pure hydrogen sulphide does not give results comparable with those obtained during actual purifying operations, and prefer to use unpurified city gas to foul the material under test. The Purification Committee of the American Gas Association is attempting to standardize procedure for this method of testing but at the present time no such standardized procedure exists. The usual practice is to place the oxide, mixed with soft wood shavings or other carrying material, in a small purifier. This purifier may contain only a few quarts of the mixture, or it may be large enough to hold a few bushels. Unpurified gas is passed through the material at a rate usually from two to four times that common in practical operation. The rate of flow and volume passed are determined by a small gas meter following the purifier. It is customary to compare two oxides, the characteristics of one of which are quite well known, in two purifiers, side by side. The rates of flow through the boxes are kept equal, the gas being measured by separate meters. Determinations of the amount of hydrogen sulphide in the gas issuing from the purifiers are made at their outlets. In some cases the test for each material is stopped when the gas passing through that material shows a stain on lead acetate paper held in the gas stream at the outlet of the purifiers. The relative volume of gas passed up to the time a certain end point is obtained is considered a measure of the usefulness of the material.

10. *Choice of Testing Method.*—The method employed for testing purifying material depends to a great extent on the viewpoint of the operator and the specific information he wishes to obtain. The tests with pure hydrogen sulphide are usually short, intensive, and comparable, but not under conditions exactly similar to those existing in plant practice. The tests with city gas are usually long, variable, and not comparable, except in cases where two or more oxides are tested at the same time under one set of conditions; the results obtained cannot be compared with the performances of other materials tested at other times or under other conditions. The use of city gas

introduces variables which are difficult if not impossible to control over an extended series of tests; therefore, where the object is to compare the particular properties of a number of oxides, the tests with pure hydrogen sulphide are much more convenient, and probably quite reliable.



## V. TESTING METHOD EMPLOYED IN PRESENT INVESTIGATION

11. *Information Desired.*—The object of the present investigation was the determination, if possible, of the primary capacities of various materials in terms which would be directly comparable, even although the actual results obtained could not be exactly reproduced in practical operation. Tests of oxides as ordinarily conducted do not really give much definite information as to the relative activity of the oxides. This characteristic probably changes during the useful life of a given material, and this change of activity may be affected, in practical operation, by a number of uncontrollable conditions. For the purpose of the present investigation, therefore, it was felt that the activity test should be made as short as possible and under conditions which could readily be controlled.

12. *Method Employed.*—The Kunberger test previously described seemed most convenient for the purposes of the proposed study, but with some modification. In the Kunberger test the oxide sample is fouled for one hour, alternate foulings and revivifications being repeated as often as desired. In general, this method of treatment will give some idea of the activity of a particular material. It will show whether the material revivifies quickly or slowly, and how complete the foulings and revivifications are; but, since all but the very slowest materials foul almost completely in one hour, this test does not show the comparative rapidities of the various materials.

The first step in studying the activity of oxides, was to determine how long the fouling of materials actually continued when an excess of pure hydrogen sulphide gas was present in contact with them. Selected materials were fouled for 10 minutes. It was found that the amount of hydrogen sulphide decomposed in this time was almost as great as the amount decomposed in one hour. It was then decided to make foulings of one minute duration, keeping the tubes well stoppered to prevent revivification while they were being weighed between foulings. It was found that differences in rapidity, or activity, which were not detectable with longer fouling periods were

quite evident in the results obtained with the shorter foulings. The foulings were conducted in practically the same manner, the gas being passed through the material at a rate sufficient to insure an excess of hydrogen sulphide present in contact with the material at all times.

13. *Oxides Tested.*—The oxides tested were principally commercial purifying materials obtained from several different oxide producers. They included oxides of all three types previously mentioned, viz., precipitated, natural ore, and rust oxides. Table 1 shows the sulphiding properties of the oxides tested. The oxides of the first two classes were mixed with sawdust in the ratio of 4 grams of oxide to 2 grams of sawdust. Of the ready mixed rust oxides, 6 grams were used for each test, no shavings being needed. The rust oxides were ground in a coffee mill before use, to about the same degree of fineness as the sawdust used with the other oxides. Each mixture of oxide was moistened with 2 cc. of water to make the oxide adhere to the sawdust. Since it was anticipated that moisture might have some

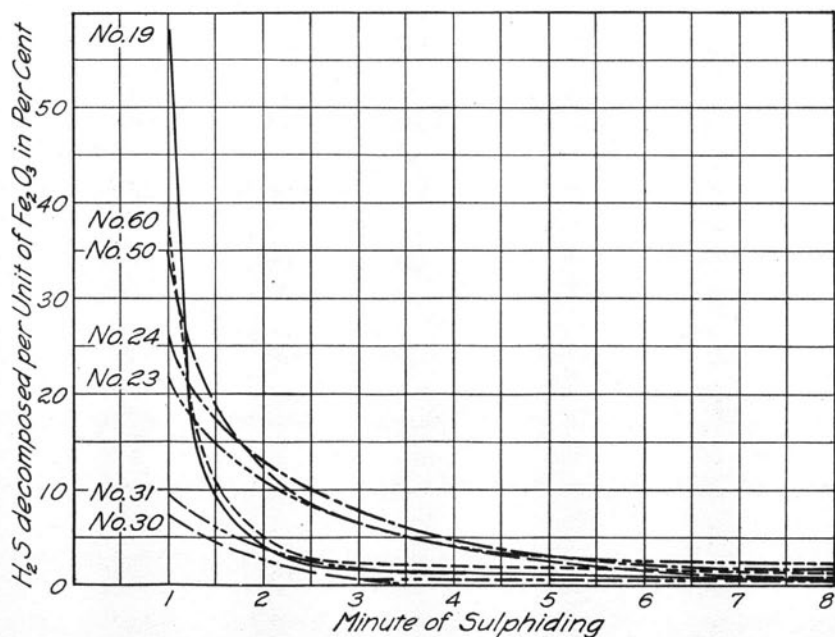


FIG. 2. DECOMPOSITION OF HYDROGEN SULPHIDE BY VARIOUS IRON OXIDES DURING SUCCESSIVE MINUTES OF SULPHIDING

TABLE 1. SULPHIDING PROPERTIES OF VARIOUS OXIDES

KIND OF OXIDE	SOURCE	LAB. No.	MOIST-URE UP TO 105° C.	DRIED AT 105° C.		AS RECEIVED H <sub>2</sub> S DECOMPOSED PER CENT						H <sub>2</sub> S DECOMPOSED PER UNIT Fe <sub>2</sub> O <sub>3</sub> PER CENT			H <sub>2</sub> S DECOMPOSED, PER CENT OF, THEORETICAL, FOR ONE FOULING*		
				Fe <sub>2</sub> O <sub>3</sub> Per Cent	H <sub>2</sub> O Re-main-ing Per Cent	1 Foul-ing	2 Foul-ing	3 Foul-ing	4 Foul-ing	5 Foul-ing	6 Foul-ing	1 Min. Foul-ing	1 Foul-ing	4 Foul-ing	1 Foul-ing	4 Foul-ing	6 Foul-ing
Precipitate	Commercial	19	22.8	39.8	15.9	19.9	21.8	18.6	12.2	13.9	13.0	58.4	63.9	236.0	31.2	113.6	....
	"	21	5.9	41.8	8.3	26.7	23.2	18.4	7.6	....	....	48.2	63.9	176.0	41.8	119.0	....
	"	23	7.0	65.0	15.8	36.9	30.2	26.6	9.9	....	....	40.2	58.2	163.0	57.8	162.2	....
	"	24	3.4	73.5	8.8	44.6	30.4	14.1	7.9	....	....	39.5	62.0	134.5	70.0	152.0	....
Rust	"	26	46.7	65.0	15.1	20.6	12.4	11.4	4.5	....	....	13.9	59.5	141.1	32.3	76.6	....
	"	28	16.8	73.4	11.4	16.1	9.5	8.9	5.4	....	....	10.5	24.6	61.0	25.2	62.5	....
	"	30	16.8	72.5	11.3	13.3	7.5	5.0	4.0	3.7	3.4	15.0	22.5	42.2	20.8	46.7	57.8
	"	31	11.8	78.1	....	13.1	9.2	6.7	5.2	6.1	5.9	8.3	16.7	49.5	20.5	53.6	72.4
Precipitate	Laboratory	40	0.0	90.0	10.0	36.4	21.2	16.7	19.3	19.4	9.5	18.4	40.5	104.0	57.1	146.8	192.0
	Commercial	50	7.1	38.4	8.8	22.2	....	....	....	....	....	56.1	62.7	....	34.8	....	....
	Laboratory	51	10.1	25.4	21.1	17.9	....	....	....	....	....	57.5	45.5	....	28.0	....	....
	"	54	8.5	19.9	3.0	11.6	....	....	....	....	....	58.6	63.8	....	18.2	....	....
Rust	Commercial	56	20.4	54.2	17.1	18.3	....	....	....	....	....	38.0	44.7	....	28.7	....	....
	Laboratory	58	0.0	93.2	6.8	50.0	41.9	20.8	24.8	28.1	18.6	22.0	53.6	157.0	78.3	229.5	311.0
	"	60	4.7	72.3	17.2	34.2	....	....	....	....	....	48.8	50.1	....	53.6	....	....

\*As discussed in the text, the numbers in these columns represent percentages of the amount of H<sub>2</sub>S that would be decomposed, theoretically, by the same weight of pure Fe<sub>2</sub>O<sub>3</sub>, during one complete fouling.

effect on the activities of the materials, care was taken to use the same amount of water in all the samples.

Fig. 2 shows the results obtained from this test of the various oxides. Oxide No. 19 is a commercial precipitated oxide, obtained by treating an iron-bearing mine water with finely ground limestone. Oxide No. 60 is a naturally precipitated material formed when the iron dissolved in certain waters is deposited by hydrolysis. This particular oxide was obtained in the laboratory from the action of condensed steam on the interiors of the iron pipes through which it flowed. The oxide was present in the water as a flocculent yellowish-brown precipitate and was separated by filtration and dried at room temperature. Oxide No. 50 is one obtained from the decomposition of bauxite by fusion with alkali and subsequent treatment of the melt with water. Oxides Nos. 23 and 24 are natural-ore oxides, while oxides Nos. 30 and 31 are commercial iron-borings oxides.

As is evident from the curves, the differences in the activities of the various oxides are much greater during the first minute of exposure to hydrogen sulphide than during successive minutes. Some oxides decompose during the first minute of contact with hydrogen sulphide nearly all of that gas that they can decompose during one fouling, while others act much more slowly. While it has not been possible to check up these relative activities on a practical scale, it seems probable that an oxide which is able to decompose nearly the amount of hydrogen sulphide corresponding to its ferric oxide content in one minute would be especially effective for use in a catch box where an oxide capable of removing small amounts of hydrogen sulphide is needed. One of the more rapid of these oxides has been used in a water-gas plant having a computed overload of about 70 per cent during the hour of maximum production, and in that case, at least, the material demonstrated its ability to completely purify the gas under conditions which overtaxed oxides of other types employed. The activity of an oxide is of course but one factor governing its usefulness, and it is possible to prepare a material which is very rapid but which has very low capacity.

Since the activity of a material is affected by the concentration of hydrogen sulphide present in the gas to be purified, and since the ability of materials to rapidly decompose traces of hydrogen sulphide governs to a great extent their usefulness in a catch box, a study of the behavior of various materials under conditions simulating those

found in practice would give valuable information if carefully controlled. Unfortunately, the activity is affected by factors which are difficult to control over a long test, and it was therefore decided to adhere to the short test just described.

Since the various materials thus far examined had shown such marked differences in properties, it was decided, if possible, to determine some of the chemical and physical conditions underlying these differences. The first step was a search of the literature to determine what had already been done by previous investigators.

## VI. PREVIOUS WORK

Since the inception of the use of iron oxide for purifying gas, numerous reports of work carried on in the investigation of various phases of the subject have appeared. By far the larger number of these contributions have had to do with methods of purifying materials in the plant, and the disposal of spent oxide. Comparatively little has been written, so far as a search of the literature reveals, concerning the factors which immediately affect the sulphiding and revivifying reactions, and the physical and chemical principles upon which the behavior of oxides depends.

Fulwiler and Kunberger\* carried on some experiments with purifying oxides which seemed to go a long way toward the explanation of the peculiarities of certain oxides. They tested a variety of oxides, both commercial and laboratory samples, and concluded that the efficiency of oxide is dependent upon the state in which it exists; that the most efficient state is that known as the reversible hydrogel, and that it seems impossible to prepare such material artificially without a protective colloid. Fulwiler and Kunberger give a somewhat lengthy discussion of colloids, which makes their conclusion more intelligible to the average reader than it would be otherwise. The terms which they employ are rather difficult to define in a few words. The exact physical nature of ferric oxide in the form of a hydrogel is not known, but we may assume that it has "a spongy or honeycomb-like structure and retains more or less water." A reversible hydrogel is one which can under favorable conditions go back into an apparent state of solution, while an irreversible hydrogel does not. A protective colloid is a substance like gelatine, glue, starch, etc., which under certain conditions can go into an apparent state of solution and which when present with other reversible colloids keeps them in the reversible state. Fulwiler and Kunberger made many attempts to prepare ferric hydroxide in the form of a reversible hydrogel, but state that they were not very successful; the materials produced with protective colloid retained their activities to hydrogen sulphide some-

---

\* Proc. Amer. Gas Inst., Vol. 8, pt. 1, p. 476, 1913.



what better than materials prepared otherwise, but no commercial method of preparation was evolved. They recognized that the activity of iron oxide is a function of the surface exposed, and that in general oxides having the largest specific volume are most active. They were inclined to the opinion that water of hydration had no direct effect on the activity of oxides, but assisted by keeping the material in the active state.

Geoffrey Weyman\* holds to the idea that ferric oxide forms a complete series of hydrated oxides stable within a very narrow range of temperature and vapor pressure conditions. He attributes the activity of ferric oxide for hydrogen sulphide absorption to its molecular state, and regards the amount of water of hydration as of bearing only in that it affects the internal arrangement of the molecule. Mr. Weyman states that oxides attain their greatest activity when dried for several hours at about 600 deg. C. His definition of activity is the percentage of hydrogen sulphide absorbed per 100 grains of the ferric oxide ( $\text{Fe}_2\text{O}_3$ ) present, divided by the theoretical amount (63.9%) with which ferric oxide is capable of combining. It should be noted that this conception of activity is different from the idea of activity which has been developed in this bulletin. Mr. Weyman also made a considerable study of the reactions taking place during the sulphiding and revivifying of oxides.

---

\* Gas Journal, Vol. 150, p. 256, May 4, 1920.

## VII. EFFECT OF WATER CONTENT ON THE BEHAVIOR OF OXIDES

14. *Hydration of Iron Oxides.*—From the reports just referred to it seems evident that these investigators recognized that the water content of an oxide had at least an indirect bearing upon its reaction with hydrogen sulphide. Their absorption tests with various oxides seem to have been carried on for too long a time to distinguish between the different rates of fouling of various oxides, since all but the slowest oxides will foul practically completely in one hour. Weyman did observe differences in water carrying capacities of some oxides as affecting their behaviors with hydrogen sulphide, as will be noted later.

In practical purifier operation the effect of excessive or insufficient moisture in oxides is frequently observed, but just what percentage of moisture is desirable in a given material or how to preserve the proper percentage for best operation is a difficult matter to decide. Even if the proper amount of water is present in the material when it is put into the purifier, the water deposited or taken away by the gas is likely soon to upset this favorable condition. Just what part the water present plays in the action of the oxide has long been discussed by gas operators and differing views are held.

It has long been a question for debate among gas chemists, and indeed among chemists generally, just what form of union exists between iron oxide and water. It has been generally recognized that iron oxides retain a certain amount of water with great tenacity. A sample of hydrated iron oxide may be heated to a temperature several hundred degrees centigrade above the boiling point of water, and after exposure to such temperature for several hours it will still yield moisture upon ignition at a red heat. Some chemists are not satisfied that all the water is expelled from iron oxide unless the material is ignited to constant weight with a blast lamp. Since it is generally assumed that all surface moisture is expelled from materials upon exposure for a few hours to a temperature slightly above 100 deg. C., it is natural to infer that water remaining after such drying is combined water rather than surface water; indeed, it is a well known fact that some chemical compounds lose a portion of their

combined water at temperatures even below 100 deg. C. The idea has been held, therefore, by some, that iron oxide may form a series of hydrates of definite composition, each stable under certain conditions of temperature and vapor pressure; and it has frequently been conjectured by those who are interested in the use of oxides for gas purification that, were it possible to prepare and keep oxides in the form of the higher hydrates, such forms of oxide would be more active agents for purifying gas than the lower hydrates or non-hydrates to which the compositions of most commercial oxides more or less approximately correspond. The idea of the existence in nature of a series of hydrated oxides of iron has been fostered by the tabulation in various books on mineralogy of a series of hydrated iron oxides. Those usually listed, with the chemical compositions assigned, are as follows:

NAME	FORMULA	PER CENT WATER
Turgite.....	$2 \text{ Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	5.1
Goethite.....	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	10.1
Hydrogoethite....	$3 \text{ Fe}_2\text{O}_3 \cdot 4 \text{ H}_2\text{O}$	13.0
Limonite.....	$2 \text{ Fe}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$	14.5
Xanthosiderite....	$\text{Fe}_2\text{O}_3 \cdot 2 \text{ H}_2\text{O}$	18.4
Limnite.....	$\text{Fe}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$	25.3

Of these, goethite alone has well defined physical and chemical properties. The other names in the list have been given because of certain indefinite physical differences, associated with plausible but not well established chemical formulas.

In the effort to establish the existence of these compounds, a number of investigators have attempted to prepare them synthetically. Directions for accomplishing this are given in some of the older reference books of inorganic chemistry. The writer attempted the preparation of these hydrates but found, just as previous investigators had discovered, that while it was possible to obtain materials approximating the theoretical compositions and physical properties assigned to these hydrates, it was extremely difficult, if not impossible, to prepare materials which had the exact composition, and were stable under normal conditions. Incidentally, these attempts at the preparation of various hydrates gave a variety of oxides of known composition to work with in the attempt to correlate water content of oxides with their activities as hydrogen sulphide absorbers.

After much experimenting had been done, and the literature of the subject quite thoroughly reviewed, there was found a reference to some work by Posnjak and Merwin\* of the Geophysical Laboratory of Washington. From some very careful work carried on over a period of several months, these investigators concluded that no series of hydrates of ferric oxide exists among the natural minerals; that the existing hydrate is the monohydrate; and that no definitely crystallized synthetic hydrates of ferric oxide have been prepared up to the present time. They feel certain that only two distinct types of "amorphous" hydrated ferric oxide exist: one yellow, and the other reddish-brown. The yellow is apparently essentially ferric oxide monohydrate, while the reddish-brown substance may hold its water in either dissolved or an adsorbed condition, or both. Thus the synthetic and natural hydrated ferric oxides exhibit, chemically, great similarity.

While it does not seem that the gas engineer can look for any improvement in the activity of iron oxides by the preparation of higher hydrates of definite composition, this does not prove that the water held by oxides has no effect on activity. It has been observed frequently that an oxide which has been overheated during preparation or during revivification, and has been thereby deprived of most of its water content, has its activity greatly impaired, and it has been generally recognized that certain natural bog ores with a high water content are particularly active. The idea that the water is in some form of combination with the iron oxide is quite natural, for it has been observed that oxides which have been dehydrated at a high temperature rehydrate very slowly if at all. If the water were merely surface moisture such behavior would hardly be expected. Since the water content of an oxide obviously plays a part, even though indirectly, in determining the activity of the oxide for decomposing hydrogen sulphide, it was decided to study this effect.

#### 15. *Effect of Water Content of Various Oxides on their Relative Activities and Capacities.*

##### **Determination of Water Content**

The method used in determining the water content of the oxides examined depended upon their composition as determined by chemical

---

\* American Journal of Science, Vol. 47, pp. 311-358, 1919.

analysis. The impurities present in simple oxides prepared in the laboratory are known. In such of these materials as contained water as the only volatile constituent, the water content was determined by loss on ignition. In other oxides, both laboratory and commercial, which contained sulphates which might decompose, the water was determined by the Rose-Jansch Method. A gram of the oxide was mixed with several times its weight of a previously dried mixture of litharge and lead peroxide. The charge was placed in a short hard glass tube, together with a layer of dried lead peroxide from which it was separated by a wad of ignited asbestos. The lead peroxide layer was kept hot by a small bunsen burner. The mixture of iron and lead oxides was strongly heated with a Meker burner until it melted. During ignition a slow current of air, previously dried by passing through a U-tube containing calcium chloride, was passed over the charge, and the water taken up from the iron oxide and carried forward in the air current was collected by another calcium chloride tube which had previously been weighed. The gain in weight of this tube during the ignition gave the weight of water in the oxide sample.

Some iron oxides, especially those commercial materials made by rusting iron in contact with shavings, contained much woody material. Since it was desired to estimate the amount of water present with the oxide itself as distinguished from the water formed by decomposition of the wood, the procedure with such materials was somewhat different. The samples were first dried at 105 deg. C. One portion of the sample was burned in a tube furnace by a current of dry oxygen, oxidation of hydrocarbons formed being accomplished by copper oxide. Water and carbon dioxide were determined by absorption in calcium chloride and potassium hydroxide in the usual manner. Another portion of the sample was treated with dilute hydrochloric acid to dissolve the iron present and the residue after drying at 105 deg. C. was burned in the manner just described. The water derived from the wood could thus be determined, and the carbon dioxide determination afforded a check on the result, being approximately the same in both cases per unit of original dried sample.

#### Preparation of Samples for Drying

The samples of natural and precipitated oxide were used in the same state of division as when received. The rust oxides, which were received as manufactured, viz., precipitated on shavings, were air

dried and then ground in a coffee mill. The ground material was somewhat coarser than the natural oxides.

#### Drying of Samples

In order to determine the effect of the varying water content in these materials, under approximately comparable conditions, 10-grain samples were weighed out into weighing bottles, which were afterwards placed in a large vacuum desiccator over concentrated sulphuric acid. The atmosphere of the desiccator was exhausted to as high a vacuum as could be obtained with a large filter pump; the vacuum was not measured. The samples were left in the desiccator several weeks with the lids off the weighing bottles. At intervals of a few days the lids were replaced, and the samples were weighed, this procedure being continued until a constant weight was attained for each sample. It was thought that possibly by this method of drying the surface water could be got rid of without expelling some of the more essential water which would be removed presumably at a higher temperature.

#### Activity and Capacity of Dried Samples

The dried samples were analysed for moisture and iron content, and tested as to their activity and primary capacity for decomposing hydrogen sulphide. Table 2 shows the results obtained. From this table it will be observed that different oxides have widely different water contents when dried under the same conditions. An attempt has been made in Fig. 3 to plot the activity and capacity of the various materials in relation to their water content.

In order to use the same system of ordinates throughout, the capacities have been expressed in percentages of hydrogen sulphide decomposed per unit of ferric oxide. This might be termed "unit capacity." The relative capacities of various oxides would of course depend upon their iron oxide contents as well as their unit capacities. To obtain the capacity of an oxide for purposes of comparison it would be necessary to multiply the unit capacity by the percentage of ferric oxide present.

It will be observed that while in general there appears to be some relation between water content and activity, there are a number of points which fall far from the curve. As for capacity, the water content apparently has little effect on this property, except that the



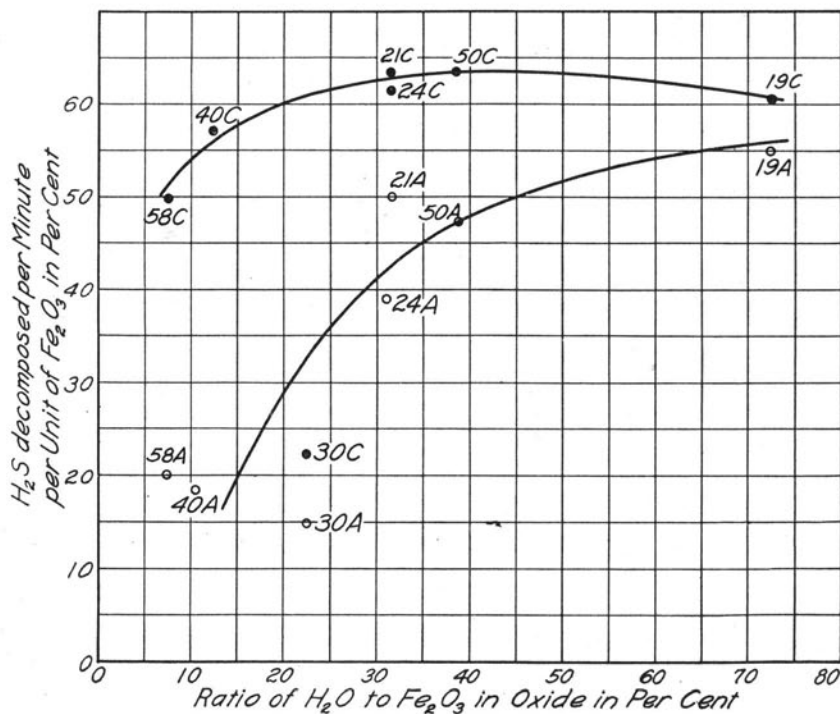


FIG. 3. ACTIVITIES AND CAPACITIES OF VARIOUS OXIDES AFTER DRYING TO CONSTANT WEIGHT

NOTE—Points marked "A" denote activity in percentage of hydrogen sulphide decomposed per minute per unit of ferric oxide; points marked "C" denote capacity of oxide for decomposing hydrogen sulphide during one fouling, in percentage of hydrogen sulphide per unit of ferric oxide, no oxygen being present in the gas.

rate of the reaction is so greatly retarded in some cases that for practical purposes the capacity is decreased. The probable reason for certain observed discrepancies will be discussed later in this paper.

16. *Effect of Varying Water Content on the Behavior of Different Oxides.*—Since there appear to be marked differences in the physical structures of oxides, it was thought that the effect of water content could be determined best by varying the water content of individual oxides and determining the effect upon their activities.

The water content, activity, and capacity per unit of ferric oxide of each material in the condition as received or prepared were first determined. A sample of several grams was then partially dried

TABLE 2.

WATER CONTENT AND SULPHIDING PROPERTIES OF VARIOUS OXIDES AFTER DRYING TO CONSTANT WEIGHT.

No.	KIND	Water Content of Oxide as Received	Water Content of Dried Oxide	Fe <sub>2</sub> O <sub>3</sub> Content of Dried Oxide	Ratio H <sub>2</sub> O: Fe <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> S Decom- posed in 1 Min. per Unit of Fe <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> S Decom- posed in 1 Hour per Unit of Fe <sub>2</sub> O <sub>3</sub>
		Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
19	Precipitated commercial	34.0	25.4	35.3	72.0	55.0	60.0
21	Natural ore	13.4	12.7	40.0	31.8	50.0	63.9
24	Natural ore	21.3	19.8	64.0	31.0	39.0	61.6
30	Rust commercial	24.0	20.8	64.0	22.5	15.0	22.6
40	Precipitated laboratory	10.0	9.6	91.4	10.5	18.4	40.5
50	Precipitated commercial	14.8	14.1	36.1	39.0	47.2	60.3
58	Precipitated laboratory	6.8	6.8	92.2	7.3	22.0	53.6

and the water content, activity, and capacity of the dried material determined. A portion of the material was set aside in a glass stoppered bottle and the remaining portion dried further, after which the same determinations were made. This process was repeated until a series of perhaps five or six sets of values had been obtained. The last drying was usually accomplished by heating the oxide in a drying oven for several hours at 105 deg. C. A few samples were heated to a higher temperature. The ratio of water content to ferric oxide content was computed in each case. The hydrogen sulphide decomposition per minute and per hour per unit of ferric oxide were calculated and the results plotted as shown in Fig. 4. The oxides examined included several of those previously tested, as shown in Fig. 1, and some other materials subsequently prepared or received.

Upon inspection of Fig. 4, it will be observed that each material has a particular water content or range of water content at which the activity of the material is at a maximum. In some cases the maximum is very definite, as in the case of oxide No. 58. In other samples, as No. 54, the maximum is very indefinite, extending over a considerable range. The great difference in the slopes, maximum points, and shapes of the various curves in Fig. 4 indicates that there are marked differences in the physical conditions of the various materials, which



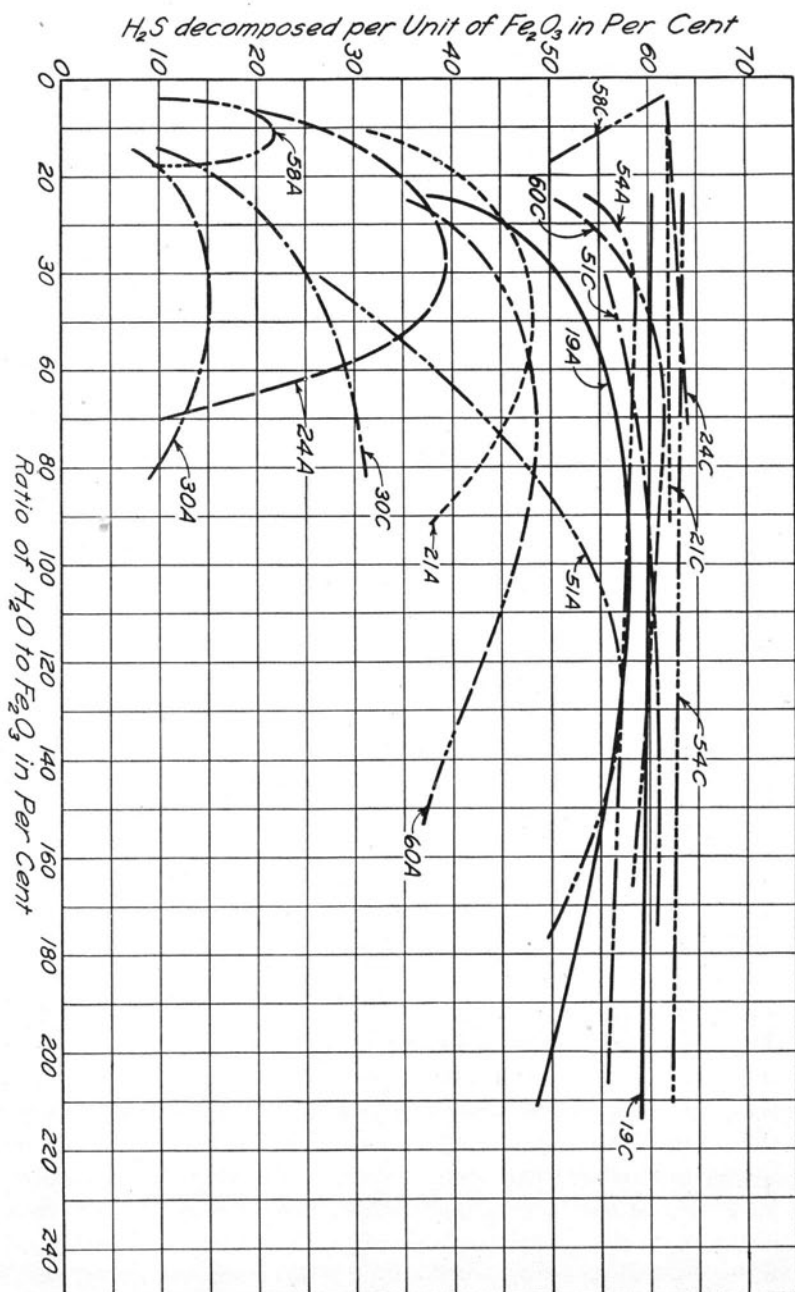


FIG. 4. EFFECT OF WATER CONTENT UPON ACTIVITY AND CAPACITY OF OXIDES

NOTE—Curves marked "A" denote activity in percentages of hydrogen sulphide decomposed per minute per unit of ferric oxide; curves marked "C" denote capacity in percentages of hydrogen sulphide decomposed per hour per unit of ferric oxide.

greatly affect the influence of water content on their activities in decomposing hydrogen sulphide. Some of these physical differences are apparent upon inspection of the materials. In general, the more active materials are of lower specific gravity, are more porous in appearance, and are usually of lighter color than the less active materials. While color is probably but incidental to the state of division, it seems to be roughly indicative of the activity. The very active materials are usually yellow in color when in the condition as received or prepared. Upon heating the materials the color deepens, passes usually through an orange or brown shade, then through brick red, and finally, upon ignition over a Meker burner, generally becomes a deep red or black. The less active materials vary in color all the way from reddish brown to brick red, and upon heating the color becomes darker. In the report of Posnjak and Merwin, previously mentioned, it is stated that iron oxide monohydrate with or without adsorbed water is usually of yellowish or brownish color, whereas the non-hydrate is red; and that the so-called amorphous prepared oxides, while apparently having no definite water content, exhibit properties similar in this respect to those of the natural materials. This being true, the natural inference is that the more active oxides contain either the monohydrate iron oxide or the amorphous forms of oxide corresponding to it, whereas the less active materials contain non-hydrate. In this connection, the definition of activity as used in this bulletin should be borne in mind, since almost all of these materials are able to absorb nearly the theoretical amount of hydrogen sulphide, granted that sufficient time is allowed.

It is evident from the curves of Fig. 4 that the materials have widely different capacities for water with respect to the maintenance of high activity. The reason for this seems to be found in their physical state. The opinion is held that more active materials generally have a greater capacity for water on account of the enormous surface of material exposed. If water be added to these materials, it is distributed over so large an area that within certain limits it has small effect in excluding the hydrogen sulphide gas. Indeed, in some cases, the mere addition of water to the oxide increases its activity, possibly by catalytic effect, making portions of the surface damp which would otherwise be too dry to react quickly. In the case of the less active oxides the surface exposed seems to be smaller. The addition of water to such oxides, except within rather narrow limits, causes the

pores of the material to be filled up so that they become water-logged, so to speak, and the rapid reaction of hydrogen sulphide with the surface of the material is prevented.

The decrease of activity experienced when an oxide is dried so that it contains less than the most favorable amount of water, seems to be caused by contraction of the surface. By this contraction, apparently, the pores of the material are closed up to a certain extent, and the result is that the hydrogen sulphide has a smaller area with which to react. Given sufficient time, the hydrogen sulphide seems to be able to penetrate through the outer surface of the oxide and react with the inner portion of the material, but activity, apparently, is directly dependent on the surface exposed, and thus the very rapid oxides are those which have a large surface in proportion to their weight.

In Fig. 4, curve No. 30, which was obtained from a commercial rust oxide, appears to indicate an exception to the rule just stated. The material, however, contained much unruined iron, and therefore, since the hydrogen sulphide decomposition is based upon the total iron content expressed as iron oxide, the position of the curve is lower than it would otherwise be. Moreover, in oxides containing much free iron it is very difficult to get a representative small sample, on account of the high specific gravity of the iron, and it is quite possible that this helps to account for the low position of the curve. Curve No. 60, which was obtained from tests of a rust oxide produced under conditions which gave complete oxidation of the iron, lies much higher, indicating that rust oxides may be quite active if produced under favorable conditions.

17. *Function of Water Present.*—As has been pointed out previously, it is very doubtful whether iron oxide forms a series of definite hydrates; but the relation between the iron oxide and the water seems in many cases to be of a much more intimate nature than would be expected if the water were merely surface moisture. Probably the phenomenon of adsorption (not absorption) is effective in such cases. By adsorption is usually understood the concentration of liquids or gases upon the surface of a solid material. This phenomenon is especially marked when the surface is very large in proportion to the volume. Hydrogen sulphide is in a measure soluble in water; and it is possible that adsorption increases the concentration of the

solution of hydrogen sulphide in water upon the surface of the iron oxide, resulting in an increase in the rate of the reaction between the hydrogen sulphide and the iron oxide. In this sense the water may be regarded as a primary solvent of hydrogen sulphide. Another view of the function of the water is that it acts as a catalyzer, directly promoting the reaction between the hydrogen sulphide and the iron oxide.

18. *Rehydration of Oxides.*—Since the drying of oxides to a water content below a certain favorable amount results in a decrease of activity, it is desirable to learn what effect re-moistening would have on this property. To determine this, a sample of oxide was dried in stages, and the activity and moisture content were determined at each stage. The lowest moisture content was reached by drying the oxide for two or three hours at about 400 deg. F. Equal weights of the driest material were then moistened with different amounts of distilled water and the activity and the water content of each portion were determined. The results are shown in Fig. 5.

As was anticipated, the activity values of the moistened samples did not follow the curve drawn through the values obtained during

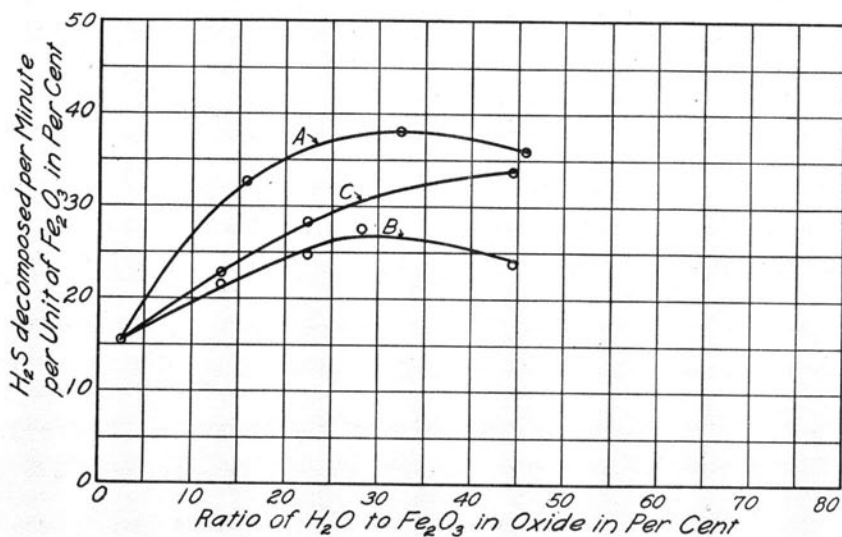


FIG. 5. EFFECT OF DRYING AND REMOISTENING UPON THE ACTIVITY OF AN IRON OXIDE

the drying process. Curve A was obtained from tests of the dried samples, Curve B from the remoistened samples tested within a few hours after preparation, and Curve C from the moistened samples tested three days later. Except during the brief time necessary for removing material for tests, the samples were kept in glass stoppered weighing bottles.

From Fig. 5 it will be observed that the curves for the remoistened materials are lower than those for the dried material; but that Curve C, obtained after the moistened samples had stood for three days, is higher than Curve B. From this it appears that after three days the moisture had, to a considerable extent, assumed its former relation to the iron oxide. Apparently considerable readsorption had taken place, whereas the samples immediately after moistening contained the water in a less intimate relation with the iron oxide. It is also interesting to note that the recovery of activity in the case of the more moist samples was more rapid than in the case of the samples of smaller water content.

The driest sample used in obtaining the curves of Fig. 5 was prepared by heating the oxide a few hours at 400 deg. F. (205 deg. C.). Since Posnjak and Merwin have shown that the decomposition of ferrie oxide monohydrate is very slow at temperatures near the decomposition temperature (about 200 deg. C.), it is unlikely that the decomposition of this sample was anywhere near complete. Since it was desired to compare the relative activities of hydrates and non-hydrates, the experiment was repeated, using a natural hydrated oxide of iron, and carrying on the final dehydration for several hours at 400 deg. C. It was assumed that at this higher temperature the decomposition would proceed more rapidly and be complete within a few hours. The sample to be decomposed was heated several hours at this temperature in a glass tube contained in an electrically heated furnace. A current of dried air was passed over the sample during the heating. The temperature was measured by a high-reading nitrogen-filled thermometer, the bulb of which was in the center of the oxide mass. The weight of oxide dehydrated was only about 10 grams, so there was little possibility of great differences in temperature throughout the mass. The decomposition of the oxide was indicated by the color change from yellowish brown to deep red. After this treatment, the water content and the hydrogen sulphide decomposition activity of the oxide, designated B, were determined. The same determinations

had been made meanwhile on the undried sample, designated A. To obtain information on intermediate states, and to study the rehydration of the decomposed oxide, samples of the original oxide were reduced to varying degrees of dryness, and samples of the dehydrated material were moistened. After some hours the water content and activity of each of the various materials were determined.

If some irregularities, probably due to experimental error, be allowed for, the outstanding difference between the results of this experiment and those shown in Fig. 5 is that, apparently, the monohydrate of ferric oxide having been decomposed, does not reform; or at least, if the oxide does eventually rehydrate in the presence of water, this rehydration takes place so slowly that it was not appreciable during the experiment. The activity of the original oxide decreased rapidly upon drying, the activity of the hydrate was distinctly greater than that of the non-hydrate, and the latter did not regain its activity appreciably after being re-moistened. The natural conclusion is, therefore, that activity due to the presence of adsorbed moisture, if lost by drying, can be gradually restored in the presence of water which can be readsorbed by the oxide, but that activity possessed by the hydrate due to combined water is regained very slowly if at all, after the decomposition of the hydrate, by drying at a high temperature if the resulting non-hydrate is moistened.

The amounts of hydrogen sulphide decomposed in one hour by the various samples were also determined. It was observed that while there was a considerable difference between the amounts decomposed by the hydrate and the non-hydrate, probably due to the great difference in rapidity of hydrogen sulphide decomposition, the intermediate samples showed no consistent variation in this respect, and that, therefore, the capacity differences shown may be largely accidental.

19. *Effect of Sulphiding and Revivifying on the Water Content of Oxides.*—The question has often been raised as to what effect sulphiding and subsequent revivification has on the water content of oxides. Some have maintained that the regenerated oxide does not hydrate, though the chemical equations given as representing the reactions taking place sometimes assume the rehydration of the oxide.

An experiment was carried out to determine if possible the facts in the case. A yellow hydrated natural-ore oxide was dried several



hours at 400 deg. C. The color of the oxide changed from yellow brown to deep red. A one gram sample of the original material and a one gram sample of the partially dehydrated material resulting from the drying at 400 deg. C. were placed in an oven at 105 deg. C. for several hours to expel any surface moisture that might be present. The water contents of both materials were then determined by fusion with lead oxides and collection of the water liberated in a weighed calcium chloride tube, as previously described. Both materials were then moistened slightly and sulphided with hydrogen sulphide, care being taken not to allow the temperature to become excessive. The sulphides produced were further moistened slightly and allowed to stand several hours in the air. Both samples revived and practically resumed their original colors, the material which had been a hydrated oxide regaining its yellow brown, and the other sample, which was apparently a non-hydrate, its original deep red. The materials were afterward dried several hours in an oven at 105 deg. C., and the water content of each was then determined; following are the results obtained:

	HYDRATE PER CENT	NON-HYDRATE PER CENT
Fe <sub>2</sub> O <sub>3</sub> content.....	66.8	90.1
H <sub>2</sub> O content before fouling.....	18.02	6.24
H <sub>2</sub> O content after fouling and revivifying.....	12.35	5.82
Ratio H <sub>2</sub> O : Fe <sub>2</sub> O <sub>3</sub> before fouling.....	27.0	6.9
Ratio H <sub>2</sub> O : Fe <sub>2</sub> O <sub>3</sub> after fouling and revivifying.....	18.5	6.4

Since the ratio of water to ferric oxide in monohydrated oxide of iron is 11.25 per cent, it is evident that sufficient moisture remained in the material in the first case to form the hydrate. The fact that the material resumed its former appearance would also indicate the probability that rehydration took place. This is somewhat at variance with the conclusions of Weyman.\* The non-hydrate on the other hand did not hydrate during revivification, although plenty of water was undoubtedly present to enable it to do so. Both samples showed smaller water contents after revivification than before, but this may have been a difference in the adsorbed moisture. It seems possible that successive sulphidings and revivifications may result in a gradual contraction of the materials, resulting in a smaller surface and consequently decreasing the power of adsorption. This contraction might be expected to have an effect on the activity of the material which would correspond with the observed behavior.

\* Gas Journal, Vol. 15, p. 256, May 4, 1920.

## VIII. ACTIVITY AND CAPACITY OF OXIDES AFTER REVIVIFICATION

The activity results thus far discussed have been obtained from tests on fresh materials. The value of an oxide for gas purification is determined, however, not only by its activity and capacity when new, but by the degree to which it retains these properties after having been in use for some time. The operating practice in gas plants is to sulphide and revivify the oxide alternately. Even in cases where a small percentage of air is continually pumped into the gas, it is unlikely that sulphiding and revivification are going on simultaneously in any given part of the material. As seen from equations (3) and (4) previously given, free sulphur is one of the products of the reaction, and accumulating as it does in the mass of oxide, it tends eventually to coat the active oxide and retard its activity. The activity and capacity of various oxides after the first sulphiding and revivification vary as greatly as before the first sulphiding. Some materials actually decompose more hydrogen sulphide on the second than on the first sulphiding, and may continue for several successive foulings to decompose amounts which vary but little from that decomposed on the first occasion. Other oxides fall off in capacity very rapidly after being used once. Indeed, it is not unusual to find oxides which are almost worthless after one fouling. In such cases, the perplexing question is, of course, whether the material itself is inferior, or whether the method of handling is responsible for the failure.

In order to determine the effect of sulphiding and revivification upon the activity of oxides, successive tests were made on three oxides of different types. Oxide No. 19 was a commercial precipitated material, No. 24 was a natural-ore oxide and No. 31 was a commercial rusted-borings oxide. Each oxide was first dried at 105 deg. C. for about two hours. The amounts of hydrogen sulphide decomposed by each oxide in one minute and in one hour were determined. The samples were next revivified by passing through them slowly for 24 hours air which had been moistened by bubbling through water, and were dried again by passing over them a current of dried air while they were kept at 105 deg. C. The sulphidings were then repeated. The results obtained from four successive tests of each material are shown in



Fig. 6. Owing to the fact that all samples were dried at 105 deg. C., in order to have a common basis for comparison, all the activities recorded are lower than would have been the case had it been practicable to compare the materials in a more hydrated condition. As might be expected the activities of all the oxides decreased with successive foulings under the same conditions of drying. In general the capacities per fouling also decreased.

These changes in the oxides seem to be due partly to the gradually accumulating content of free sulphur, which coats the surface, and thereby partially excludes the hydrogen sulphide, and partly to the increasing incompleteness of the revivifications. Failure of the oxide

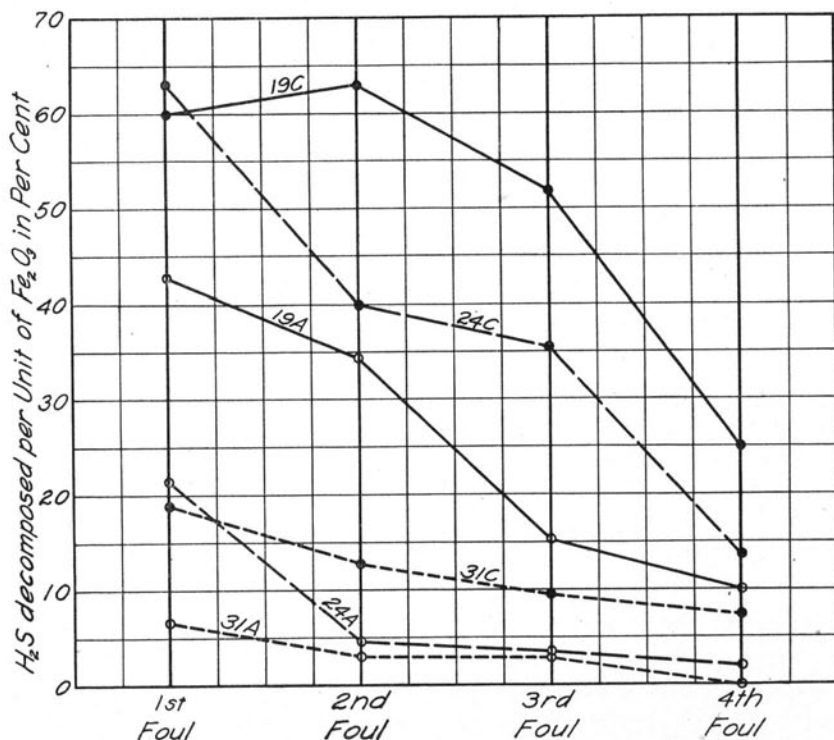


FIG. 6. ACTIVITIES AND CAPACITIES OF THREE TYPICAL OXIDES DURING FOUR SUCCESSIVE FOULINGS

NOTE—Curves marked "A" denote activity in percentages of hydrogen sulphide decomposed per minute per unit of ferric oxide; curves marked "C" denote capacity in percentages of hydrogen sulphide decomposed per unit of ferric oxide during one complete fouling.

to completely revivify might be due to two causes: (1) inability of the oxygen of the air to gain access to the iron sulphide on account of the free sulphur; and (2) the formation of sulphides which do not readily revivify. It is probable that both these conditions are responsible for the deterioration of oxide in laboratory tests, whereas in plant operation the presence of tar vapors and cyanides in coal gas further tends to the coating of the active material and the formation of inert compounds, thus hastening the deterioration of oxide.

## IX. EFFECTS OF CONDITIONS OF PREPARATION ON ACTIVITY OF OXIDES

It is evident from the results given that there are many different degrees of activity found in oxides. It is also evident that water content alone is not responsible for the differences in behavior shown by various commercial and prepared materials. It seems apparent that it is mainly the physical and chemical structure of an oxide that determines its activity; but that, the structure being once determined, water content does have a bearing on the behavior of the material. In the case of natural-ore oxides we must take the materials as they exist. The oxides may be put into a somewhat finer state of division by grinding, their surface and activity being somewhat increased thereby; but the activity seems to depend chiefly upon the structure of the material which can not be readily altered by any means at our disposal.

In the case of precipitated materials, whether formed by the precipitation of ferric hydroxide from solutions of iron salts, or by the rusting of metallic iron, which is essentially solution and subsequent precipitation, we have more control over the character of the product formed. Just why certain methods of precipitation result in precipitates of a certain character may not be easy to explain, but the efforts to make in the laboratory oxides of different degrees of water when dried at 100 deg. C., and pulverizes very readily to a fine which had widely differing characteristics and which had been produced under known conditions. Comparing the behaviors of these materials with the behaviors of typical commercial products, we may draw some conclusions as to how the latter were formed.

The characteristics of practically all of the commercial oxides examined lie between those possessed by two types of precipitated oxides. One of these types is represented by the material produced when a concentrated solution of a ferric salt is precipitated either hot or cold by ammonium hydroxide, and the reddish-brown precipitate, after washing, is boiled with water about 100 hours. The resulting oxide is brick-red in color, retains only about three to six per cent of water when dried at 100 deg. C., and pulverizes very readily to a fine powder. This oxide is nearly pure ferric oxide and has a large primary

capacity for decomposing hydrogen sulphide. It is very slow to get into action as is shown by curve No. 58, Fig. 4.

A precipitate similarly obtained, but dried in the air without the long boiling, shrinks and cracks and finally, when dried in air at 105 deg. C., is a hard horn-like substance almost black in color. This precipitate usually contains about 18 per cent of water and pulverizes with considerable difficulty to a gritty reddish-brown powder, which reacts but slowly with hydrogen sulphide, decomposing only about 16 per cent per unit of ferric oxide.

As an example of the other type, if a concentrated solution of ferric or ferrous sulphate be precipitated with finely ground calcium carbonate, a light yellow or yellowish-brown precipitate forms which, when dried in air, pulverizes readily to a yellowish powder, which may contain about 28 per cent of water. This precipitate reacts with hydrogen sulphide very rapidly. (See curve No. 51, Fig. 4.) A similar precipitate with a larger iron content is obtained when a dilute solution of a ferrous salt is allowed to oxidize in air. By hydrolysis and oxidation a ferric oxide (or hydroxide) is found which has a yellowish or yellowish-brown color. When dried in air it may retain about 22 per cent of water, and in this condition is able to react with hydrogen sulphide very rapidly. Such a precipitate is also obtained when iron is slowly rusted by water and the iron is precipitated by hydrolysis. (See curve No. 60, Fig. 4.)

If we consider the various commercial oxides, we find that they resemble these prepared materials both in appearance and behavior. The yellowish or yellowish-brown materials produced commercially by the precipitation of iron-bearing mine waters by hydrolysis and the use of finely ground limestone (calcium carbonate), as typified by oxide No. 19, show great rapidity. Some of the yellowish-brown natural oxides are also similar in behavior, as shown by curve No. 21. The red oxides of iron, so far as have been examined, are not so rapid. Sample No. 24 is an example of the better grade of red ore oxides. It will be observed that it decomposes only about half as much hydrogen sulphide per unit of ferric oxide in one minute as does sample No. 19, yet it has a much greater primary capacity, since it decomposes in 1 hour about the same amount of hydrogen sulphide per unit of ferric oxide and its ferric oxide content is much greater than that of No. 19. Sample No. 30 is a commercial rust oxide. The finer particles were of a yellowish-brown color, but there was a large proportion

of larger particles which were hard and nearly black. These large particles appeared to have a grain of unoxidized iron as a nucleus, and resembled greatly the dense hard material formed by drying a ferric hydroxide precipitated by ammonia from a concentrated solution as previously described. The presence of these hard granular particles was apparently responsible for the comparatively low activity of the material, and they made it so slow in action that it was not able to decompose more than a small percentage of its theoretical capacity. The indications were that this, as well as other commercial rust oxides, had been prepared in such great haste that not only was insufficient time allowed for oxidation, but precipitation had taken place from comparatively concentrated solutions on the surface of the iron, resulting in the hard, compact, and relatively inactive form of oxide previously mentioned. It is also possible that overheating had occurred during the rusting process.

## X. PREPARATION OF COMMERCIAL OXIDES

The relation of conditions of preparation to the properties of commercial oxides can best be made clear by brief descriptions of some of the processes employed in producing oxides for the gas industry. Some gas operators manufacture their own purifying materials, but lack of space, high cost of labor, and the attention required to obtain a good product are usually such obstacles that many gas plants buy their oxide sponge (iron oxide and shavings) ready mixed. In some cases certain natural or prepared oxides are purchased and mixed with shavings at the plant. This is a simple process compared with the procedure sometimes resorted to, of producing the oxide by rusting iron in contact with shavings. Usually the preparation of rust oxides is left to regular oxide manufacturers. The production of material in large quantity makes it feasible to use machinery for handling to an extent not possible in the case of the average gas plant. The following are general methods employed in preparing typical materials. The procedures described are by no means fixed; modifications of the various processes are doubtless made by different manufacturers.

20. *Natural Oxides*.—Weyman\* divides these into two classes, namely, bog ores and degraded iron ores. The former he states is essentially ferrous hydroxide precipitated on peat fibre. On exposure to the air it oxidizes to the ferric form. When this material is dried at but little above ordinary air temperature, nearly all of the oxide is active. Owing to the extremely fine state of division and large surface covered by the oxide it is particularly effective. He further states that the porosity and area covered by the oxide make it possible to have present a large amount of water without the activity being much affected. In the curves of Fig. 4 no true bog ore is represented. The characteristics attributed to it, however, especially the ability to carry a large amount of water without impairing the activity, agree well with the characteristics shown by some of the oxides produced by somewhat different processes, as No. 19 and No. 60.

---

\* Gas Journal, Vol. 150, p. 256, May 4, 1920

Degraded iron ores Weyman defines as those produced by the weathering of exposed iron ores or rocks containing iron. He states that they cannot carry as much water as bog ores without loss of efficiency; that fine grinding gives larger surface and accelerates the rate of absorption (or activity, as defined in this report) but cannot increase the activity or approach the activity of bog ore. In connection with this statement it should be noted that the term "activity," as used by Weyman, corresponds rather closely to "capacity" as used in this report. Oxides Nos. 21 and 24 would probably fall under Weyman's classification of iron ores.

In plant practice these natural ores are usually mixed with planer chips (oak chips must not be used since the wood acids form with iron oxide compounds inactive to hydrogen sulphide), ground corneobs, or other porous materials, before being put into the purifiers. Under favorable conditions natural oxides do good work, but where there is an overloaded condition of the purifying equipment, natural ores, especially of the second class, do not seem to be rapid enough to remove all of the hydrogen sulphide from the gas. It is difficult to control the amount of moisture in the oxide, not only during preparation but also during operation, and this factor doubtless has a marked effect on the usefulness of the material. If it is either a little too wet or a little too dry the activity is seriously affected, and with so narrow a range of activity the probability that the moisture content will not be most favorable is very great.

21. *Precipitated Oxides.*—Various products which might be classified under this head are on the market. Indeed, rust oxides might strictly be called precipitated oxides, since solution of the iron and subsequent deposition of the oxide doubtless take place. As discussed here, however, precipitated oxides will include only those in which the principal portion of the oxide is derived from a solution of an iron salt by treatment with certain reagents. The first manufactured oxides for gas purification were made from copperas, or ferrous sulphate. One formula for the preparation of such an oxide is as follows:

"To each bushel of shavings use 25 pounds copperas, 5 to 6 pounds of lime, and 1 pound of rusted iron borings. The copperas is dissolved with hot water or steam. The lime and water are mixed in a separate container thin enough to be sprinkled with a sprinkling can. The



shavings are spread on the ground in a layer of about 18 inches thick. The iron oxide, or rust, is spread over the shavings and sprinkled with half of the copperas solution. Then half of the lime is sprinkled over the layer and it is turned with forks or shovels. The next day the remainder of the copperas and lime is added and the material is shoveled over again, and daily thereafter until the material remains cool."

The precipitation of the iron in this case is accompanied by deposition of calcium sulphate which dilutes the mixture, but may be of some advantage mechanically by separating the particles of iron oxide and preventing them from coalescing. The iron oxide is probably added to increase the iron content without correspondingly increasing the amount of calcium sulphate, as would be the case if more iron were added in the form of the sulphate. Steere says that oxide made from copperas acts more quickly than natural oxides and is apparently at its highest efficiency after one revivification. Oxides Nos. 19 and 51 in Fig. 4 were prepared in a manner somewhat similar to that described except that no free iron was used. No. 19 was precipitated commercially by calcium carbonate from the ferrous and ferric sulphates present in certain mine water, while No. 51 was precipitated from a solution of ferric sulphate by calcium carbonate. In Fig. 6 it will be noted that oxide No. 19 had its greatest absorption after one fouling, which agrees with the statement just referred to, if, as is probable, the idea of efficiency included only capacity for decomposing hydrogen sulphide.

22. *Rust Oxides*.—Steere divides rust oxides into two classes, namely, those produced by rusting clean cast iron borings with some rusting solution, such as salt, sal ammoniac (ammonium chloride), or other accelerating agent, and those oxides produced by rusting the iron with water only, applying it as a fine spray.

#### Oxidation by Rusting Solutions

In making the first class of oxides soft gray iron borings, cast iron planer chips, or turnings, clean and free from steel, oil, or rust, are usually employed. Borings must pass through a  $\frac{1}{4}$ -inch mesh screen and chips or turnings must break up readily. Wood shavings, or some other form of carrier, are spread on the floor in a layer about one foot thick. The iron borings in the proportion of about 25 to 30



pounds per cubic foot of shavings (the proportions may vary) are spread evenly over the shavings. The bed is then sprinkled thoroughly with the rusting solution (one quart of salt in a barrel of water), and the materials are thoroughly mixed immediately after sprinkling. The mixing is repeated daily while it continues to heat, and oftener if overheating is threatened. The beds should be sprinkled with water daily and kept damp. A little more salt solution is added occasionally if oxidation appears slow. The oxidizing process requires about one week. Special care should be taken to avoid overheating. This material is said to be at its best the first time it is used.

Of the oxides tested, No. 30 appears to represent this class. It contained a high ferric oxide content (72.5 per cent) and might therefore be expected to have a large potential capacity for decomposing hydrogen sulphide. As shown by Table 1 and Fig. 4, however, the material did not give results in keeping with this expectation. The decomposition of hydrogen sulphide per unit of ferric oxide was low and decreased on successive foulings. Under the laboratory test the material did not have the opportunity of lying exposed to the weather for weeks at a time, as is frequently the case in practice; this exposure probably assists to some extent in oxidizing and hydrating the material. An examination of the material indicated partially the reason for its poor performance. While part of the iron oxide present was in the form of a fine brownish powder, a considerable part of it was in comparatively large particles. Each of these larger particles which were of very compact appearance, and had a nearly black surface color, seemed to contain a nucleus of free iron, since they were attracted by a magnet. They resembled the oxide resulting from drying the precipitate formed by treating concentrated ferric solutions with ammonia. The cause of this condition cannot be stated with certainty. It seems likely that overheating took place during oxidation, or that possibly the speed of the rusting process was such that it resulted in precipitation from a concentrated solution, giving the kind of precipitate observed.

While with the conditions obtaining in practice, such a material might show some improvement with time, it seems quite as likely that depreciation due to tar and other impurities in the gas would tend to occur at a more rapid rate. In spite of the fact that the mixture is rich in ferric oxide, it shows less than half the capacity on four foulings that is shown by some other materials with only half the

ferrie oxide content. It may be possible to make good oxide by the accelerated rusting process, but it is believed that the attempt to hasten production frequently results in a deterioration of quality. Other oxides of a similar nature were examined, and the results obtained were not very different. (See Table 1, Oxide 31, which was prepared by a different producer.)

#### Oxidation by Water

This process of manufacture seems to have been gaining favor among several of the larger gas companies during recent years. The usual procedure is to mix thoroughly the desired amount of iron borings with shavings or other carrier and spread the mixture to a depth of 10 to 12 inches on level ground. A sufficient number of lawn sprinklers are then arranged to keep the material moist without producing any considerable washing effect. The sprays are kept going night and day unless the weather is such that the material will remain moist over night. The mixture is turned every two or three days. Showering is continued until oxidation is complete, and heating does not occur; this usually requires from three to four weeks. The material is then ready for use or can be stored.

Among the commercial samples studied by the writer, there were included no bona fide samples of water-rusted oxide. One or two samples were supposed to have been produced by some modification of this process, but their behavior indicated that they had been very imperfectly rusted, or that the materials selected were not of the best. Laboratory sample No. 60 (see Table 1 and Fig. 4) probably represents very closely what might be expected of a thoroughly rusted material of this type. The rusting in this case really consisted of solution of the iron by water and subsequent deposition, the deposition taking place in a container into which the iron-bearing water was allowed to drip. As will be observed from Fig. 4, the oxide had good activity and capacity per unit of ferrie oxide, and the activity remained fairly great over a considerable range of water content. The material seemed to occupy a place midway between the precipitated and natural oxides previously described.

23. *Pyritic Cinder*.—The iron oxide resulting from the burning of pyrite ( $\text{FeS}_2$ ) has been used to some extent for gas purification. None of the commercial oxides submitted for study were of this type.

Pyritic cinder may be quite high in ferric oxide content, containing 85 per cent or more, and if active would presumably have a high capacity for decomposing hydrogen sulphide. On account of the high temperature at which it is produced, it is dehydrated and sometimes partially fused. Weyman, in the article previously referred to, states that pyritic cinder is slower than bog ore, denser, and requires working at a higher temperature. It is also slower in revivification. The same is true of oxide recovered by burning the sulphur out of spent oxide. Such material is said to be even less active than pyritic cinder, probably because it is subjected to high temperatures for a longer period.

## XI. CHOICE OF OXIDE.

The choice of material to be used in any particular plant will depend upon a number of conditions. One of the conditions to be considered is the load factor. A plant in which the rate of purification must necessarily be very great during certain portions of the day will evidently need a more rapid oxide than one in which the gas can be passed through the purifiers slowly and at a uniform rate. As has been shown, most of the better oxides will take up their full capacity of hydrogen sulphide, providing adequate time is given, but where the time of contact is very short, some of them may fail to remove all of the hydrogen sulphide from the gas. Another condition to be considered in connection with the activity of a material is the effect of moisture upon its behavior. The curves of Fig. 4 illustrate this condition, and it seems that in practical operation it might well be given greater consideration. As has been already shown the activity and to a lesser degree the capacity are affected by the moisture content of the oxide. In practice this is a difficult thing to control. If a material is put into the purifiers too dry it will not react rapidly, while if too wet the rapidity of the reaction is also impaired. Moreover, the moisture content of the oxide may change greatly during use. The gas does not always carry a uniform moisture content. If the temperature of the gas drops on its way through the purifiers water will be deposited, or, if the gas is unsaturated at the temperature of the purifiers, water will be taken away from the oxide. The sulphiding reaction liberates water from the oxide. The water formed by this reaction, together with water deposited by the gas, may become excessive and diminish the rapidity of the purifying material. Water has an especially retarding effect upon the rate of revivification, and where revivification in place is practised, an excess of moisture in the oxide may cause slowness in the rate at which the revivification takes place. It would seem then that oxides, the activities of which are least affected by water, would be most practical for overloaded plants, especially those in which the overload was caused rather by the high rate of purification necessary, than by excessive sulphur content of the gas. This might be the case in some overloaded water-gas

plants. It seems likely that the failure of many of the natural-ore oxides can be attributed not to any lack of capacity for handling hydrogen sulphide, but rather to the fact that their condition of active operation is limited to a very narrow range of water content, which is very difficult or impossible to control in practice.

The very active oxides would find great usefulness in catch boxes, where the function of the material is to remove small amounts of hydrogen sulphide from the gas at the high rates of purification sometimes necessary. For such work speed in action and in revivification would appear to be the qualities most required.

The capacity factor must not be left out of consideration, by any means. The experiments made appear to indicate that it is almost necessary to sacrifice capacity in order to obtain high activity, or vice versa. The very active oxides usually have a high capacity per unit of iron oxide, but the iron oxide content is usually low. For example, oxide No. 54 contains when carrying its most favorable water content, only about 21.7 per cent of ferric oxide. Since the theoretical decomposition of hydrogen sulphide is 63.9 per cent of the ferric oxide content, it is evident that such a material could absorb less than 14 per cent of its weight of hydrogen sulphide in one fouling. Therefore, a bushel of sponge, containing, say, 30 pounds of oxide to the bushel, could purify during one fouling not more than 29 000 cubic feet of gas containing 100 grains of hydrogen sulphide to 100 cubic feet. With gas of a higher sulphur content the capacity would be further reduced. On the other hand, consider one of the slowest materials tested, No. 58. This oxide absorbed approximately 60 per cent of hydrogen sulphide per unit of ferric oxide, and its ferric oxide content was 93.2 per cent. A bushel of sponge containing 30 pounds of this oxide would purify approximately 119 000 cubic feet of gas of the same hydrogen sulphide content in one fouling. Neither oxide No. 54 nor No. 58 were commercial products, but they appear to represent extreme types of purifying materials. Obviously the ideal material would be one which combined the properties of both these oxides. The fulfillment of such a condition seems unlikely. The activity of materials typified by oxide No. 54 seems to be due to their large surface and this condition of large surface seems to be made possible by the inert materials such as calcium sulphate, etc., which prevent the separate particles of oxide from coalescing. These inert substances of course increase the weight and necessitate the use

of a greater amount of the material to provide a given amount of active oxide. Oxide No. 58 is almost pure ferric oxide, but, in the absence of any inert constituents to separate the individual particles, the material is denser and slower in action. In oxide No. 60 we have a compromise. The material at condition of greatest activity and capacity contains about 76 per cent of ferric oxide. A bushel of sponge made up in the same proportions as previously suggested would purify about 98 000 cubic feet of gas per fouling. Its activity would be greater than that of No. 58, and be less affected by moisture content; on the other hand, moisture would affect it more than oxide No. 54.

Another point to be considered in the choice of oxide is the efficiency which it retains after several foulings. In most cases the more active oxides retain their efficiencies better than the slower materials. As will be seen in Table 1, the capacities of certain oxides over six foulings were determined. No. 54 was not studied to this extent, but the results shown for No. 19 are probably quite similar. The capacity for six foulings is expressed as percentage of the total amount of hydrogen sulphide which would be decomposed, theoretically, during one fouling by pure ferric oxide. This serves as a standard by which to compare materials of different oxide content. It will be noted that the performance of oxide No. 19 was 155.7 per cent of the standard, while No. 58 was 311.0 per cent. When it is considered, however, that No. 19 contained only 39.8 per cent of ferric oxide on a dry basis, and No. 58 contained 93.2 per cent on the same basis, the difference is not so remarkable. It will be noted that the absorption by No. 19 for six foulings was five times as great as for one fouling, whereas the absorption by No. 58 was 3.97 times as great for six foulings as for one. It is evident, therefore, that No. 58 loses its capacity much more rapidly than No. 19. The capacities of these two materials are so different on account of the disparity in ferric oxide content that it is likely that they would reach the same capacity only after many more foulings. In the case of some materials whose characteristics are more nearly alike, however, six foulings might be sufficient to determine relative capacities.

Whether six foulings, more or less, would be sufficient in comparing oxides would also depend upon other circumstances. It would obviously be useless to base performance on six foulings if plant conditions were such that the material was practically spoiled with

tar after being in the purifiers only three or four times. It would seem unwise, also, to use a material of exceptionally high ferric oxide content and low activity under conditions where it is almost certain that only a small part of the oxide will come into use. It is to be remembered that a purifier box is seldom emptied because the contained material is completely fouled. The reason for emptying is almost always that the activity has decreased to such a degree that more hydrogen sulphide is passing forward to the other purifiers than the activity of their contained material will permit them to handle at the rate of gas flow prevailing. It would appear, therefore, that a material which is able to absorb a large percentage of its theoretical capacity in a short time, or which in other words is very active, granted that its capacity is reasonably large, would be decidedly more efficient in a majority of plants under present conditions than a slower material of much larger capacity.



## XII. SUMMARY OF CONCLUSIONS

All of the experimental work, leading to the conclusions of this bulletin, was performed in the laboratories of the University of Illinois. It would be very desirable if some of these experiments could be checked by operation on a commercial or semi-commercial scale. Taking the laboratory experiments, the conclusions of other investigators, and experience gained in gas plant operation as a basis, the following conclusions seem justified:

(1) The usefulness of iron oxide for gas purification depends upon its physical, and perhaps upon its molecular, structure, rather than upon its iron content.

(2) There are two factors which determine the value of a particular oxide: namely, (a) the rapidity or activity of the oxide for decomposing hydrogen sulphide, and (b) the ultimate capacity of the material for decomposing hydrogen sulphide under the operating conditions.

(3) No generally accepted definitions for activity and capacity of oxides have been formulated. Tentative definitions are given in this bulletin.

(4) As defined in this publication the capacities of some oxides, per each fouling, and, to a greater degree, the activities of the oxides, are affected by their water content.

(5) It is unlikely, as shown by recent researches, that ferric oxide forms any hydrates of definite composition other than the monohydrate ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). It is doubtful whether even this definite compound exists among the synthetic oxides commonly used in gas purification, though many of the synthetic oxides resemble the natural hydrated oxides in physical and chemical properties. Therefore, the water which affects the behavior of oxides as gas-purifying agents, is probably water adsorbed on the surface of the material.

(6) For every oxide there appears to be a best water content at which the material is most active in decomposing hydrogen sulphide. If the water content be increased or decreased from this point the activity of the oxide decreases.



(7) The best water content varies with different oxides. The lighter, more porous oxides retain a high activity over a greater range of water content than do the denser and more compact materials. The reason seems to be that above a certain water content peculiar to each oxide, the water excludes the hydrogen sulphide from acting readily with the material.

(8) In general, considering oxides of all types, compared under the same conditions of drying, those materials which retain the most water are the most active.

(9) Of the various materials examined, those of a yellow or yellowish-brown color are generally more active than the red or reddish-brown oxides. The former are generally more porous in appearance, of lower density, and of higher water content than the latter, and retain their activity over a considerably greater range of water content.

(10) All the yellow or yellowish-brown oxides are transformed into the red or reddish-brown varieties by heating a few hours at 400 deg. C. The activity of the oxide decreases as a result of this transformation and is restored very slowly, if at all, by remoistening; nor does the color return to its former value, at least within several weeks, if ever. The activity lost by heating an oxide a few hours at 200 deg C. is to a considerable degree regained by remoistening the oxide and allowing it to stand several days.

(11) Oxides produced by the precipitation of ferric salts from concentrated solutions by alkaline hydroxides or carbonates, and subsequent drying, and rust oxides made with the use of rusting solutions, appear to be comparatively slow in decomposing hydrogen sulphide. Such oxides appear to become still slower in action if subjected to a temperature of 100 deg. C. for several hours. The activity of these materials is generally considerably affected by a comparatively small variation in water content.

(12) Oxides precipitated from ferric or ferrous sulphate solutions by calcium or barium hydroxides or carbonates, and oxides resulting from the slow rusting of iron at a low temperature and in the presence of considerable water, resemble the natural hydrated oxides of iron in color (yellow or yellowish-brown). Their activities are usually as great as or greater than

those of the natural hydrated oxides and retain their values over a rather wide range of water content.

(13) The capacities of most oxides are but little affected by water content, though in a few cases excess water slows the reaction with hydrogen sulphide to such an extent that it is completed only after a considerable time.

(14) In general, the more active oxides revivify more quickly and retain their activity over successive foulings with hydrogen sulphide better than the slower oxides.

(15) When a hydrated or non-hydrated oxide is sulphided and then revived in the presence of adequate water, it tends to return to the same appearance, physical state, color, and water content as it possessed before sulphiding.

(16) Extremes of activity and capacity do not seem to go together. Conditions which increase surface and hence activity of oxides, decrease iron oxide content and hence capacity, and vice versa.

(17) The choice of oxide for a particular gas-plant should be governed by conditions prevailing.

This investigation shows that great differences exist between iron oxides available for gas purification, with respect to their usefulness for the purpose. Good materials of each of the types mentioned have been in use since iron oxide was first employed as a purifying agent about 35 years ago. No very radical developments have taken place in the oxide manufacturing industry during that time. It is unlikely that our best available commercial oxides of today are really much superior to the best oxides originally used. Methods of manufacture have probably made possible the production of a more uniform grade of prepared products than formerly. Sources of supply have been developed which, together with the use of machinery in manufacture, have decreased the cost of production, and made good grades of oxide cheaper than they would be had the old methods still remained in use. After 35 years of oxide purification, however, there is no special type of material which is generally recognized as superior to all others. All the types of materials formerly used are still used.

Improvement in oxides for purification can only come through a thorough understanding of the effects of fundamental conditions

upon the character and performance of the product. It has not been possible in the present discussion to cover the whole range of possibilities. It has been observed by certain investigators that the presence of alkalis in oxides has an effect on their behavior out of proportion to the effects directly attributable to the alkalis themselves. This deserves study. It also seems possible that certain catalytic agents might be discovered which would increase the speed of some of the oxides of large capacity.

Oxide purification has its unavoidable limitations. A certain practical ultimate capacity can not be exceeded, regardless of the quality of the material. Spent oxide is disagreeable to handle and it is difficult to obtain labor which is willing to handle it. The sulphur in spent oxide, while often in considerable amount, can not usually be extracted profitably because of other materials present. Consequently, it is essentially a waste product. The United States imports much sulphur annually, although there is a vast amount present in this country could it be made commercially available. All coals of the United States contain sulphur. Indeed, the high sulphur content of most of the Illinois coals is a serious drawback to their use for gas and coke making, and the low-sulphur coals of other regions are steadily decreasing in amount. It appears probable, therefore, that the gas industry must eventually abandon oxide purification for some other process which involves less labor, and less space for equipment, and which produces the sulphur in a form in which it will be available for industrial purposes.

**This page is intentionally blank.**

## PUBLICATIONS OF THE ILLINOIS COAL MINING INVESTIGATIONS

- Bulletin 1.** Preliminary Report on Organization and Method of Investigations. 1913. *None available.*
- Bulletin 2.** Coal Mining Practice in District VIII (Danville), by S. O. Andros. 1913. *None available.*
- Bulletin 3.** Chemical Study of Illinois Coals, by S. W. Parr. 1916. *None available.*
- Bulletin 4.** Coal Mining Practice in District VII (Mines in bed 6 in Bond, Clinton, Christian, Macoupin, Madison, Marion, Montgomery, Moultrie, Perry, Randolph, St. Clair, Sangamon, Shelby, and Washington counties), by S. O. Andros. 1914. *None available.*
- Bulletin 5.** Coal Mining Practice in District I (Longwall), by S. O. Andros. 1914. *None available.*
- Bulletin 6.** Coal Mining Practice in District V (Mines in bed 5 in Saline and Gallatin counties), by S. O. Andros. 1914. *Free upon request.*
- Bulletin 7.** Coal Mining Practice in District II (Mines in bed 2 in Jackson County), by S. O. Andros. 1914. *Free upon request.*
- Bulletin 8.** Coal Mining Practice in District VI (Mines in bed 6 in Franklin, Jackson, Perry, and Williamson counties), by S. O. Andros. 1914. *Free upon request.*
- Bulletin 9.** Coal Mining Practice in District III (Mines in beds 1 and 2 in Brown, Calhoun, Cass, Fulton, Greene, Hancock, Henry, Jersey, Knox, McDonough, Mercer, Morgan, Rock Island, Schuyler, Scott, and Warren counties), by S. O. Andros. 1915. *Free upon request.*
- Bulletin 10.** Coal Resources of District I (Longwall), by G. H. Cady. 1915. *None available.*
- Bulletin 11.** Coal Resources of District VII (Counties listed in Bulletin 4), by Fred H. Kay. 1915. *None available.*
- Bulletin 12.** Coal Mining Practice in District IV (Mines in bed 5 in Cass, DeWitt, Fulton, Knox, Logan, Macon, Mason, McLean, Menard, Peoria, Sangamon, Schuyler, Tazewell, and Woodford counties), by S. O. Andros. 1915. *Free upon request.*
- Bulletin 13.** Coal Mining in Illinois, by S. O. Andros. 1915. *Free upon request.*
- Bulletin 14.** Coal Resources of District VIII (Danville), by Fred H. Kay and K. D. White. 1915. *Postage four cents.*
- Bulletin 15.** Coal Resources of District VI, by G. H. Cady. 1916. *Fifteen cents.*
- Bulletin 16.** Coal Resources of District II, by G. H. Cady. 1917. *Fifteen cents.*
- Bulletin 17.** Surface Subsidence in Illinois Resulting from Coal Mining, by L. E. Young. 1916. *Mailing weight, one pound.*
- Bulletin 18.** Tests on Clay Materials Available in Illinois Coal Mines, by R. T. Stull and R. K. Hursh. 1917. *Mailing weight, one pound.*
- Bulletin 19.** Coal Resources of District V, by G. H. Cady, 1919. *Mailing weight, one pound.*
- Bulletin 20.** Carbonization of Illinois Coals in Inclined Gas Retorts, by F. K. Ovitz. 1918. *Postage two cents.*
- Bulletin 21.** The Manufacture of Retort Coal-Gas in the Central States, Using Low-Sulphur Coal from Illinois, Indiana, and Western Kentucky, by W. A. Dunkley and W. W. Odell. 1918. *Postage two cents.*

## 62 PUBLICATIONS OF THE ILLINOIS COAL MINING INVESTIGATIONS

**Bulletin 22.** Water-Gas Manufacture with Central District Bituminous Coals as Generator Fuel, by W. W. Odell and W. A. Dunkley. 1918. *Postage two cents.*

**Bulletin 23.** Mines Producing Low-Sulphur Coal in the Central District, by G. H. Cady. 1919. *Postage two cents.*

**Bulletin 24.** Water-Gas Operating Methods with Central District Bituminous Coals as Generator Fuel, by W. A. Dunkley and W. W. Odell. 1919. *Postage two cents.*

**Bulletin 25.** Gas Purification in the Medium-size Gas Plants of Illinois, by W. A. Dunkley and C. E. Barnes. 1920. *Postage four cents.*

\***Bulletin 72.** U. S. Bureau of Mines, Occurrence of Explosive Gases in Coal Mines, by N. H. Darton. 1915. *Thirty-five cents.*

\***Bulletin 83.** U. S. Bureau of Mines, The Humidity of Mine Air, by R. Y. Williams. 1914. *Ten cents.*

\***Bulletin 99.** U. S. Bureau of Mines, Mine Ventilation Stoppings, by R. Y. Williams. 1915.

\***Bulletin 102.** U. S. Bureau of Mines, The Inflammability of Illinois Coal Dusts, by J. K. Clement and L. A. Scholl, Jr. 1916.

\***Bulletin 137.** U. S. Bureau of Mines, The Use of Permissible Explosives in the Coal Mines of Illinois, by James R. Fleming and John W. Koster. 1917.

\***Bulletin 138.** U. S. Bureau of Mines, Coking of Illinois Coals, by F. K. Ovitz. 1917. *Twenty cents.*

**Bulletin 91.** Engineering Experiment Station, University of Illinois, Subsidence Resulting from Mining, by L. E. Young and H. H. Stoek. 1916. *None available.*

**Bulletin 100.** Engineering Experiment Station, University of Illinois, The Percentage of Extraction of Bituminous Coal, with Special Reference to Illinois Conditions, by C. M. Young. 1917. *Free upon request.*

**Bulletin 113.** Engineering Experiment Station, University of Illinois, Panel System of Coal Mining, A Graphical Study of Percentages of Extraction, by C. M. Young. 1919. *Free upon request.*

**Bulletin 119.** Engineering Experiment Station, University of Illinois, Some Conditions Affecting the Usefulness of Iron Oxide for City Gas Purification, by W. A. Dunkley. 1921. *Free upon request.*

---

\*Copies may be obtained by addressing the Director, U. S. Bureau of Mines, Washington, D. C.

**This page is intentionally blank.**



**This page is intentionally blank.**

**THE UNIVERSITY OF ILLINOIS**  
**THE STATE UNIVERSITY**  
**Urbana**

**DAVID KINLEY, Ph.D., LL.D., President**

---

**THE UNIVERSITY INCLUDES THE FOLLOWING DEPARTMENTS:**

**The Graduate School**

**The College of Liberal Arts and Sciences** (Ancient and Modern Languages and Literatures; History, Economics, Political Science, Sociology; Philosophy, Psychology, Education; Mathematics; Astronomy; Geology; Physics; Chemistry; Botany; Zoology, Entomology; Physiology; Art and Design)

**The College of Commerce and Business Administration** (General Business, Banking, Insurance, Accountancy, Railway Administration, Foreign Commerce; Courses for Commercial Teachers and Commercial and Civic Secretaries)

**The College of Engineering** (Architecture; Architectural, Ceramic, Civil, Electrical, Mechanical, Mining, Municipal and Sanitary, and Railway Engineering; General Engineering Physics)

**The College of Agriculture** (Agronomy; Animal Husbandry; Dairy Husbandry; Horticulture and Landscape Gardening; Agricultural Extension; Teachers' Course; Home Economics)

**The College of Law** (Three-year and four-year curriculums based on two years and one year of college work respectively)

**The College of Education** (including the Bureau of Educational Research)

**The Curriculum in Journalism**

**The Curriculums in Chemistry and Chemical Engineering**

**The School of Railway Engineering and Administration**

**The School of Music** (four-year curriculum)

**The Library School** (two-year curriculum for college graduates)

**The College of Medicine** (in Chicago)

**The College of Dentistry** (in Chicago)

**The School of Pharmacy** (in Chicago; Ph.G. and Ph.C. curriculums)

**The Summer Session** (eight weeks)

**Experiment Stations and Scientific Bureaus:** U. S. Agricultural Experiment Station; Engineering Experiment Station; State Laboratory of Natural History; State Entomologist's Office; Biological Experiment Station on Illinois River; State Water Survey; State Geological Survey; U. S. Bureau of Mines Experiment Station.

The library collections contain (April 1, 1921) 490,274 volumes and 116,663 pamphlets.

For catalogs and information address

**THE REGISTRAR**  
**Urbana, Illinois**

